OCTET

Pre-Workshop Participant Statements

Some Brief Thoughts on Deep Water Formation

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Long-term change in the rate of deep water formation, in response to changes in upper ocean stratification and changes in deep circulation of the ocean, is one critical uncertainty in our estimates of ocean CO2 uptake and how it might change in the future. Rates of deep water formation may change on relatively short time scales, especially in the Greenland/Iceland/Norwegian Sea (GIN) region. Such changes may be associated with abrupt shifts in large-scale ocean circulation, such as the postulated change in the orientation of the Gulf Stream. However, the Weddell and Ross Seas, along with some regions of the Antarctic continental shelf, are also sites of deep water formation, which are affected by the extent of sea ice. The challenge for such studies is the complicated mix of time and space scales over which these processes occur as well as the low absolute velocities associated with these deep currents. For example the WOCE P15 line could just detect freon at the Samoan Passage as deep water moved northwards into the North Pacific, implying that the water had taken about 50 years to move from its formation site near Antarctica.

A research strategy must necessarily involve short-term process studies as well as longer time measurements with an eye towards improving our representation of these processes in our numerical models. A process study should focus on specific "choke points" and regions of intermediate and deep water formation such as the GIN region and the Antarctic continental shelf. Measurements should include a combination of biogeochemical and physical processes as part of deep hydrographic surveys. Given the complicated chemistry of CO2, a proxy such as freon is probably the most useful to estimate formation rates. The ability to use models to examine this behavior is problematic because at this stage, the GCMs have neither the resolution nor the physics to model continental shelf circulation and convection.

Once is Not Enough - Advocating Study of Interannual Variability of Carbon Fluxes

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JGOFS provided a snapshot of ocean carbon fluxes in regions critical to the global carbon cycle, but most JGOFS studies were unable to collect records of sufficient duration to determine the sensitivity of carbon fluxes to changes in physical forcing. Physical and biogeochemical processes influencing the ocean carbon cycle respond in complex and non-linear ways to changes in environmental conditions. Substantial interannual variability in physical forcing (environmental conditions) is known to occur in many regions, but with the exception of the JGOFS Time-Series sites and, perhaps, the equatorial Pacific Ocean, JGOFS obtained little information to define the response of carbon fluxes to this variability. Furthermore, because of the short duration of JGOFS process studies, the extensive suite of biogeochemical processes, parameters, rates and fluxes evaluated by JGOFS may not be representative of mean conditions at these sites if JGOFS process studies were conducted during periods of atypical forcing.

A report at the recent Ocean Sciences meeting (San Antonio, January, 2000) by Richard Lampitt, describing a 10-year follow-up of the North Atlantic region studied during the JGOFS-NABE program, illustrates the need for studies longer than the traditional 1-year JGOFS process study. Lampitt noted that winter mixed-layer depths in the North Atlantic varied by a factor of two in response to interannual variability in physical forcing. Intuitively, one would expect the concentration of nutrients in surface waters at the end of the winter to increase with increased depth of winter convection. One would further expect there to be a corresponding increase in the export flux of biogenic material, during the following spring-summer period, with increasing depth of winter convection. As expected, an ongoing record of fluxes collected by moored time-series sediment traps showed substantial interannual variability in these fluxes. A model forced by contemporary environmental conditions also produced interannual variability in export flux of a similar magnitude. Unfortunately, the interannual variability in export fluxes generated by the model bore no relationship to that measured by sediment traps. This case illustrates two important principles. First, our understanding of the biogeochemical response to changes in physical forcing is so poor that our models fail to capture essential elements of the carbon cycle even in well-studied regions like the North Atlantic Ocean. Second, process studies carried out by JGOFS may provide poor characterization of mean fluxes within the study region.

For reasons illustrated by the example above, the greatest advance in our understanding of the ocean carbon cycle that can be made during the next decade could well come from establishing the response of biogeochemical processes, ecosystem structure, and carbon fluxes to interannual variability in environmental conditions. Major components of the global climate system exhibit recognized patterns of interannual variability; for example, the North Atlantic Oscillation/Arctic Oscillation, the El Nino Southern Oscillation, the Pacific Decadal Oscillation, and meteorological conditions associated with the Antarctic Circumpolar Wave. Furthermore, global teleconnections between different regimes are now being explored; for example, linkages between sea ice distribution in the Southern Ocean and tropical SST have been established recently from analysis of time-series records. Future ocean carbon process studies should build upon this knowledge and design research programs that exploit these natural cycles to determine the biogeochemical response to interannual variability in physical forcing. Future process studies should evaluate parameters critical to ocean carbon flux over at least one full cycle of the organized pattern of atmospheric circulation (e.g., ENSO) that dominates interannual variability in each region of study.

Future ocean carbon studies can benefit from contemporary programs with complementary goals. Establishing the elements of interannual variability, and the teleconnections among various regions, is a high priority for the CLIVAR program. Ocean carbon studies should develop linkages to CLIVAR as source of information about physical processes that regulate ecosystem structure, biogeochemical processes, and carbon fluxes.

In addition, future ocean carbon studies should:

1) Before implementing any field program, model the response of ecosystem structure, biogeochemical processes and carbon flux to anticipated interannual variability in physical forcing;
2) Design and implement process studies covering a full cycle of interannual variability to evaluate the principal components of the regional carbon budget;
3) Compare actual fluxes to model predictions as a test of our understanding of the system;
4) Improve model parameterizations of critical processes;
5) Design and test methods for remote sensing of a sufficient number of key parameters to detect future changes in the system.

Determining the response of major components of the ocean carbon cycle to interannual variability in physical forcing provides a basis for predicting the ocean's response to climate change. An evolving view is that earth's climate system has multiple preferred modes or states, and that climate variability, whether rapid changes that occurred during the late Pleistocene or global warming, may be manifest by changes in the frequency at which recognizable states of modern climate (e.g., ENSO and NAO) are occupied. Models have also suggested that particular climate states are more likely to occur with different orbital configurations, which tends to support this view. If this hypothesis proves to be correct, then the recommended strategy of evaluating biogeochemical parameters and carbon fluxes over complete cycles of ENSO, NAO, etc. provides the building blocks with which to predict the ocean's response to global warming. Potential feedbacks, through changes in atmospheric greenhouse gases due to perturbations of the ocean carbon cycle, will be identified as well.

Narrowing the uncertainty in calcification and PIC standing stock estimates

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Calcium carbonate and the oceanic carbon cycle

Calcium carbonate sediments represent about a 1/4 of all marine sediments (Broecker and Peng 1982). The current global $CaCO_3$ production rate is ~0.6 Gtons C as $CaCO_3$ y^{-1} with ~0.3 Gt C produced in the deep sea (Milliman 1993) (see his map of surface calcite fluxes). Two other estimates of global calcification in shelf and slope waters are ~1 Gt C yr^{-1} (Morse and Mackenzie 1990) and ~1.1 Gt C yr^{-1} (Wollast 1993), almost 2X higher than (Milliman 1993).

Although considerably more complex, the overall stoichiometry of biogenic calcite production is often depicted as:

$$2HCO_3^- + Ca^{++} \text{ --> } CO_2 + H_2O + CaCO_3 \qquad (1)$$

Thus, for each mole of $CaCO_3$ produced, 1 mole of CO_2 is also released (Berger and Keir 1984), which may, or may not, be used in photosynthesis (Balch *et al.* 1996). To put these numbers into perspective, given a conservative global calcification rate of 0.6 Gt C y^{-1}, there should be approximately an equimolar amount of CO_2 produced each year. This represents ~1/8 of the fossil fuel CO_2 production, and is equal in magnitude to CO_2 production associated with timber cutting and agricultural tilling of soils (Broecker and Peng 1982). This could increase to 1/4 of the fossil fuel CO2 production depending on which estimate of global calcification one uses. $CaCO_3$ is produced in shallow waters by either coral reefs or *Halimeda* macrophytes, or in the plankton, by coccolithophores, foraminifera, and pteropods. Recent budgets suggest that calcification by deep sea and shelf plankton accounts for ~2/3 of global calcification (Milliman 1993). Wollast (1993) suggests that Milliman's (1993) numbers are underestimates due to sediment trap artifacts or underestimates of dissolution (Milliman *et al.* 1999). There is strong evidence for dissolution of biogenic $CaCO_3$ associated with biological processes such as grazing (Harris 1994; Buitenhuis and Barr 1998). It has been estimated that as much as 80% of the surface calcification is dissolved above the lysocline in this manner (Milliman *et al.* 1999).

Annual production of $CaCO_3$ represents only about 1-3% of the global marine organic carbon production (Koblentz-Mishke *et al.* 1970; Berger 1989; Milliman 1993; Longhurst *et al.* 1995) but due to extremely efficient remineralization of organic tissue by bacteria and higher organisms, $CaCO_3$ dominates carbon burial in many regions. It is generally thought $CaCO_3$ represents a progressively larger fraction of the total carbon flux as particles sink (Westbroek *et al.* 1993) (see his fig.3). Our own results from the equatorial Pacific, Arabian Sea, and Gulf of Maine suggest that calcification is usually 3-5% of the total carbon fixation. We have nevertheless observed regions of the oligotrophic central Pacific, where 50% of the carbon was being fixed into calcium carbonate.

It has long been recognized that coccoliths contribute a major portion of the $CaCO_3$ content of pelagic sediments (Lohmann 1908; Bramlette 1958) and the distribution of many coccolithophores in surface waters matches their sediment distribution (McIntyre and Be. 1967). The ratio of deposited $CaCO_3$ to biologically fixed $CaCO_3$ ranges from 14-55% (Broecker and Peng 1982; Milliman 1993)). *In terms of carbon actually reaching the ocean floor*, the global sedimentation flux of inorganic carbon from coccoliths is about equal to the organic flux. As for carbon burial in the "geological archive", the global $CaCO_3$ flux dominates organic carbon by a factor of ~6X (Westbroek *et al.* 1993).

Where are these processes or fluxes most significant?

Coccolithophore calcification is significant from the tropics to the boreal latitudes. While coccolithophores are found in the southern ocean, it is still thought that calcification in these regions is not geochemically as important. It is important to note, however, that there are virtually no direct measurements to support or refute this claim. The premise is only based on the lack of calcareous sediments in this region. Spectacular mesoscale coccolithophore blooms have received the most attention, while relatively little attention has been given to non-bloom conditions. Based on satellite remote sensing, one might conclude that temperate regions have the highest coccolithophore calcification. But this may not be true, given that coccolithophores simply live deeper in equatorial waters, and are not visible to the satellites.

Over what spatial and temporal scales must measurements be made?

Coccolithophores are patchily distributed, which has made it difficult to study them. Not surprisingly, calcification shows the same degree of patchiness. Our approach has been to do standard productivity-type casts, but to fill in between these profiles with "shot-gun" surface sampling. The microdiffusion ^{14}C technique (used to measure calcification and photosynthesis simultaneously; (Paasche and Brubak 1994; Balch *et al.* In Press)) is more time-consuming than the standard ^{14}C technique and is labor-intensive at sea. The measurements are performed after 12-24h bottle incubations. It is quite common in the Arabian Sea, Equatorial Pacific, and Gulf of Maine to see 100-200km patches of high calcification (Balch and Kilpatrick 1996; Balch *et al.* In Press; Graziano *et al.* in press).

Certainly the standing stock of calcite shows patchiness at scales similar to calcification rates. We have used a continuous optical technique for quantifying the amount of calcium carbonate in surface waters. It is based on the backscattering of the particulate material before and after dissolution of the $CaCO_3$. The high refractive index of $CaCO_3$ makes it an important component of the oceanic optical backscattering (often 15-40% of the total). This has important remote sensing consequences. An algorithm is now being tested to estimate PIC concentration from visible-band imagery, as taken by the recently-launched MODIS sensor. If this works, we will have the means to scale-up the observations of PIC standing stock to regional or global scales. Scaling-up calcification rate measurements to basin scales still remains problematic, however. The same problems confronting satellite remote sensing of primary production, certainly will impede development of a satellite calcification algorithm (Balch *et al.* 1992; Balch and Byrne. 1994; Behrenfeld 1997). It may be that a combination of isotope-based and alkalinity-based calcification measurements is the best option for understanding calcification over basins scales. Field alkalinity measurements are faster and require no bottle incubations, but the accuracy of the ^{14}C technique still makes it the technique of choice for short-term calcification estimates.

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MISSING PIECES OF THE OCEAN CARBON CYCLE PUZZLE

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A flexible research program should be implemented for upcoming studies of the ocean carbon cycle. Clearly there is the need for common long-term objectives and goals as well as a research program that is well integrated. However, the research platform for these studies should be flexible enough to benefit from the ingenuity and creativeness of individual scientists, and the research program should be receptive to novel objectives and approaches throughout its duration. In essence, there needs to be a balance between "top-down" and "bottom-up" controls so that the program can be responsive to new discoveries and changing technologies while maintaining specific goals and objectives. Listed below are several research topics that should be explored and potentially included in the OCTET science plan.

The fate of terrestrial organic matter in the ocean

Large quantities ($>5 \times 10^{14}$ g C) of organic matter in dissolved and particulate form enter the oceans each year through riverine discharge and aeolian transport. Most of this material has undergone extensive diagenetic alteration in the terrestrial environment prior to export to the ocean and is considered refractory in nature. A major mystery in the global carbon cycle is that only a small fraction of the organic matter dissolved in seawater and preserved in marine sediments appears to be of terrestrial origin. Apparently, the bulk of this material is efficiently and relatively rapidly remineralized in the ocean. Measurements of the distribution of terrestrially organic matter in seawater and marine sediments indicate that much of the oxidation of this material occurs in ocean margins. The mechanisms for the rapid oxidation of this material are largely unknown, but photochemical as well as microbial oxidation is likely important. The release of N and P during the remineralization of terrestrial organic matter could be a significant source of nutrients supporting the high productivity (~20% of global ocean productivity) in ocean margins. In addition to being the major site of long-term burial of organic matter in the ocean, it appears that ocean margins could also be a source of organic matter to ocean basins, but little is known about the exchange of materials between ocean margins and basins. These regions and critical aspects of the ocean C cycle should be the focus of future studies.

Diagenetic processes below the euphotic zone

Much of our understanding of the transformations and remineralization of organic matter is derived from measurements made within surface waters (0-100 m). However, recent respiration estimates indicate that most (>50%) remineralization of organic matter occurs in the mesopelagic zone (100-1000 m), where sinking particles undergo extensive decomposition. Recent studies indicate that transport of DOM from surface waters to the mesopelagic can be substantial, and studies of the chemical composition of DOM indicate dramatic diagenetic alterations occur in this region of the water column. This region of the ocean can be considered the largest "heterotrophic digester" on Earth. Remineralization processes in the mesopelagic result in extensive regions with reduced or depleted concentrations of dissolved oxygen. These low oxygen regions of the water column can have distinct microbial communities and processes, such as methanogenesis and denitrification. Thus, the products of metabolism in the mesopelagic can differ from those in surface waters . A major effort should be made to describe and quantify remineralization processes and C fluxes in this understudied region of the ocean.

Fundamental factors regulating organic matter remineralization

We will not have a clear understanding of the C cycle until the factors regulating the oxidation of organic matter are elucidated. Our studies need to reach beyond estimating C fluxes to grasp a fundamental understanding of the factors that control these fluxes. Several controlling factors have been investigated, such as temperature, nutrient availability and sorption to mineral and organic phases, but we are far from a comprehensive understanding of why some organic matter persists for decades, centuries and millennia. Perhaps the greatest conundrum of all is that the largest reservoir of refractory organic matter in the ocean exists as relatively small dissolved molecules. The ocean reservoir of DOC is similar in size to that of atmospheric carbon dioxide, so it is critical that we understand the mechanisms leading to the formation of refractory DOM as well as the eventual remineralization of this material. Recent studies of the chemical composition of DOM from various ocean basins and depths indicate some "universal" trends in organic matter composition that suggest common diagenetic processes among ocean basins. While there is considerably biochemical diversity in freshly-produced organic matter from regions with varied biological communities, diagenetic processing tends to erase these biochemical differences leaving refractory DOM that has many common chemical features. This is tantalizing because it suggests common processes leading to the formation of this large reservoir of refractory carbon as well as common factors regulating its remineralization. Future studies require novel approaches and techniques to help unravel the basic principles that ultimately determine the fate of organic matter in the ocean.

Notes about Benthic Processes on Shelves

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I think that benthic studies should earn an important place in OCTET field programming for the following reasons:

[Preamble--Allowing that total shelf area is 31×10^{12} m^2; roughly 40% is relict detrital; roughly 30% carbonate, and roughly 30% upwelling shelf--from Emery and Milliman]

1. **Shelf C_{org} Export.** Recent work on the NC coast, the Gulf of Maine and off S. Long Island indicate that very little C_{org} is transported off the shelf. However, carbon budgets for the Washington Shelf and the shelf off Monterey, Ca indicate a large fraction of new production does not arrive at the shelf sea floor (100 m). The Monterey Bay study is very well constrained

with primary productivity data for 10 years (Chavez), new production data (Chavez and Kudela) for 5 years, benthic measurements (Berelson) over 4 years, sediment trap data for 4 years (Pilskaln). This study shows that during the high productivity, upwelling period, 70% of the new production escapes the shelf. A similar fraction may escape the Washington shelf (Devol).

If new production on shelves is approx. 2 GT C/yr (Christensen), **0.4 GT C/yr** could be lost via shelf export just from the upwelling shelves around the world. This export is likely offshore and into deeper water.

2. **C_{org} Burial on Shelves.** C_{org} burial rate is difficult to come up with, especially for low/no accumulation shelves (relict). Washington, Monterey (Ca), Peru shelves have similar C_{org} burial rates, 5 mmolC/m^2d. If this rate is typical of this type of shelf, C_{org} burial in shelf sediments can account for a removal rate of **0.2 GT C/yr**. Some shelves are experiencing increasing deposition rates (San Pedro Shelf) because of shoreline erosion. Sites on the San Pedro shelf are burying C_{org} at a rate of 68 mmolC/m^2d---no more than half of this is sewage derived--hence C_{org} burial rate on shelves can be very large and anthropogenically impacted.

3. **Iron Production on Shelves**. We (Berelson, Coale and Johnson) were able to measure Fe fluxes from Monterey Bay sediments, the average daily flux is 4.3 µmoles Fe/m^2d. What is the Fe demand of a diatom? Is it 10 µmoles Fe:mole C or 50 µmoles Fe:mole C (Sunda)? Within that published range, Fe efflux could support 90-430 mmolC/m^2d (390-1900 gC/m^2yr) of primary production.

Also, C_{org} oxidation in sediments can mobilize Fe from Fe-oxides and enrich upper sediments with Fe-oxide. As this sediment is re-suspended, these oxides may get reduced and supply Fe to surface waters (Johnson). Positive feedback between Fe supply and C_{org} production on shelves should be studied!

4. **$CaCO_3$ Dissolution on Shelves**. We know that the current rate of CO_2 increase in the atmosphere is affecting surface ocean pH and $CO3^{2-}$ (Bates). The global rate of carbonate accumulation (Milliman) produces **0.1 GT C/yr** as CO_2. Changes in surface ocean pH may impact (lessen) carbonate production rates (Langdon).

Also, carbonate dissolution may exceed accumulation. Dissolution on carbonate platforms can occur at a rate of 10 mmol$CaCO_3$/m^2d (Walter). If this is widespread over carbonate shelves, it could titrate **0.5 GT C/yr** as CO_2. Carbonate dissolution on non-carbonate shelves can consume **0.05-0.1 GT C/yr**.

The rates that I present above are not well quantified, yet potentially important within the context of C_{org}/CO_2 cycling on very short time scales. The magnitude and uncertainty in these values suggest that margins should garner greater interest and study by our community. All the calculations and measurements I've made generally ignore river-impacted shelves (RioMar)--where certain rates (burial) could be much larger!

The items discussed above are primarily studied by benthic geochemists, but involve biological processes and physical processes to a great extent. The study of shelves must be undertaken with some time-series approach (El Nino's very different than non-El Nino on W. Coast) and should benefit from new technologies (Rutgers Leo Station; MBARI mooring stations; SeaWifs).

Strategies for Quantifying Global Ocean Carbon Dynamics in the Forbidden Zone

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Summary

The central hypothesis offered for OCTET to address is:
Particle flux and remineralization scales vary with oceanic circulation and biological regimes, and that the particle flux and remineralization scales in biologically dynamics waters (outside of the warm water environments used to calibrate the Martin et al. (1997) relationship) are significantly different from the common-used Martin parameterization.

The hypothesis needs to be addressed by both carefully planned shipboard process studies, executed in key biologically dynamic environments using the best available tools for capturing particulate matter samples from the forbidden zone. Neglected areas are the major subtropical and subpolar fronts with light up in concentration and variability (when not cloud obscured) in SeaWiFS imagery. Neglected seasons are Winter, Spring and Fall.

In addition:
It is feasible to develop and deploy **SOLO/carbon** floats for <u>autonomous determination</u> of carbon <u>flux</u> and <u>concentration</u> within the 100-1000 m forbidden zone. The float systems are robust, proven and long lived and are already measuring many of the physical parameters (T &S) required for a first order improvement of understanding the response of the biological pump to physical forcing.

Time scales:
SOLO * floats (or gliders) adapted for POC and PIC concentrations should attempt to capture the diurnal time scale.
SOLO floats (or gliders) adapted for POC and PIC flux, (with concentration senosrs) could operate in the "Argo" mode, with little impact on the Argo array and how it is designed to operate.
Flux and concentration data would be available in real time by telemetry of data via satellite to institutions responsible for data processing and then made available to the community. The system allows wide geo-graphic coverage for carbon flux assessment and is cost effective compared to traditional approaches (ships and moorings).

> ***Octet should not miss the opportunity to add significant biogeochemical value to the Argo style floats (and gliders) by adding sensors for both POC and PIC concentration and flux.***

Reasons for these statements follow.

*SOLO - Sounding Oceanographic Lagrangian Observer (Davis et al., 1999)

1. Quantifying the ocean's biological carbon pump.

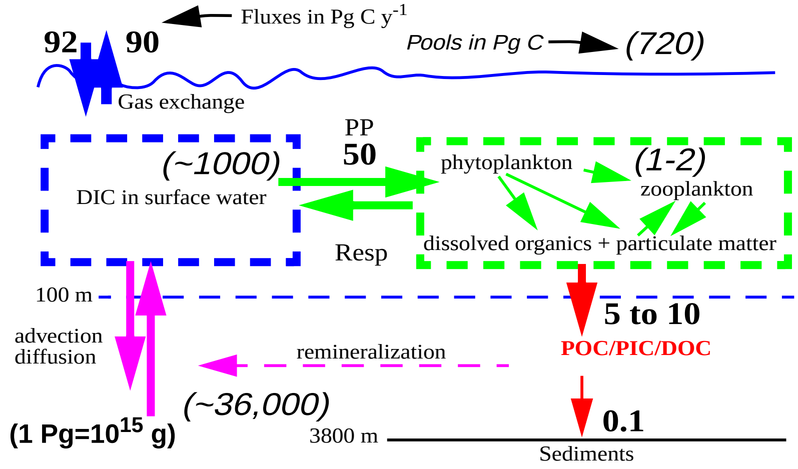

Figure 1. Fluxes and pools carbon and effects of the biological pump. A major uncertainty in the ocean's carbon cycle is the quantity of carbon exported from the surface layer and depth dependence of remineralization in the upper 1000 m. No effective ship-independent method has been yet devised to capture the temporal and vertical variability of carbon flux in these shallow waters in remote biologically dynamic ocean locations.

The biological pump (Figure 1) is the net downward transport of carbon through food-web processes (photosynthetic production of organic matter from dissolved inorganic carbon and nutrients in surface waters, grazing of the organic matter by zooplankton, downward rain of organic debris (Figure 2) and/or downward biomass migration, with subsequent remineralization/respiration of the organic carbon back to inorganic carbon at depth). This natural carbon sequestration process not only affects the levels of CO_2 in the atmosphere but also structures the organic and inorganic pools of C, N, P, O and many other chemical species in the oceanic water column. One model simulation has shown that atmospheric CO_2 would rise by over 150 ppmv without an operating biological pump (Siegenthaler and Sarmiento, 1993). Current estimates indicate that the biological pump is 10-20% efficient at moving photosynthetically fixed carbon below 100 m, but only several percent efficient below 1000 m (e.g. Honjo et al., 1995).

The oceans contain approximately 50 fold more carbon than the atmosphere and therefore could play an important role in carbon sequestration. Although marine plant biomass equals approximately 0.05% of terrestrial biomass, marine organisms photosynthetically fix an amount of carbon equal to that fixed by terrestrial plants (~50–100 Pg C/y). This seeming paradox is explained because marine plant biomass turns over on a time scale of hours to days, rather than seasons to years for terrestrial biomass. This fact makes monitoring the variability of efficiency and linkages of the biological pump with depth a major oceanographic challenge. Given the huge amounts of carbon flowing through the biological pump on an annual basis, perturbations of the pump's transport efficiency could have a major impact on carbon sequestration rates.

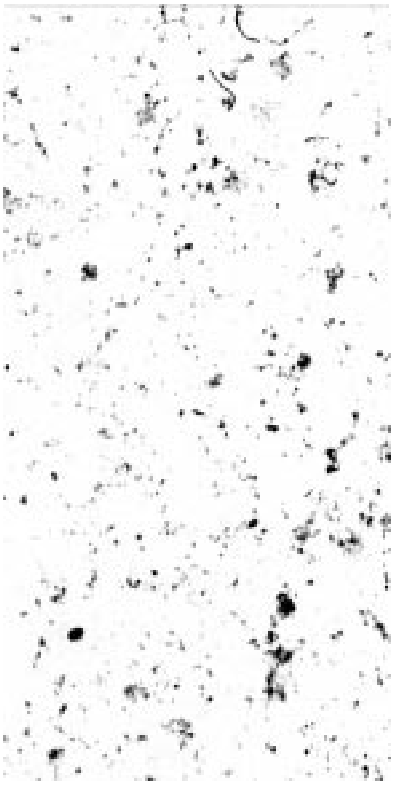

Figure 2. One to one magnified light absorption image of large particles captured by in-situ filtration at 200m in the Slope Water of the NW Atlantic. Particles shown are dominant contributors to vertical carbon flux and represent the catch from several cubic meters of seawater.

What are the consequences of climate or human induced changes in the efficiency of the biological pump on the ocean's biogeochemical cycles?

Both the biological and physical pumps may be changed in this century. Coupled atmosphere ocean simulations suggest that anthropogenic emissions of CO_2 will lead to increased stratification in the upper ocean and a lowered surface pH (Sarmiento *et al.*, 1998). Both effects would reduce the efficiency of both pumps, thereby leaving a larger fraction of anthropogenically produced CO_2 in the atmosphere. Understanding and quantifying the factors controlling sequestration efficiency and ecological consequences requires both expanded observational information and better coupled 3-D time-dependent biogeochemical/ecosystem models.

Observational limitations of shallow water carbon fluxes. A major success of the Joint Global Ocean Flux Study has been the wealth of observations of euphotic zone carbon cycle processes and of various aspects of new production (N-15) and export (Th-234 deficits, surface tethered shallow sediment traps) through 100 m. However, JGOFS did not focus on the fate of particulate matter between the base of the euphotic zone and 1000 m which is the location where most carbon remineralization occurs. A fundamental and mostly unanswered question is:

What biological, physical and chemical factors govern the export and remineralization efficiency of the biological pump?

Understanding of shallow water remineralization has relied on ship dependant methods for estimating particulate carbon fluxes: short-term deployments of surface tethered sediment traps (Knauer et al., 1979; Martin et al. 1987, Coale 1990; see also Gardner, 2000), the measurement of ^{234}Th deficit relative to ^{238}U (Coale and Bruland, 1987; Buesseler et al., 1992; Murray et al., 1996; Dunne et al., 1997, Charrette et al., 1999). and particle size-distribution/settling model calculations (eg. Bishop et al., 1987). Because of the dependence on ships, data on shallow fluxes are severely limited in space and time. Thus, carbon remineralization is currently best summarized by the pre-JGOFS Martin et al. (1987) relationship which was calibrated using 6 trap deployments (from 14N to 35N and 108W to 155W) in the NE Pacific Ocean (Eq. 1):

$$J_z = J_{100} / ((z/100)^P) \qquad (1)$$

Where J_z is carbon flux at depth z (in meters) and J_{100} is the carbon flux measured at 100 m. P, the power, is held constant at 0.858.

JGOFS time-series stations at Bermuda (BATS, Michaels and Knap, 1996) and near Hawaii (HOTS; Karl and Lucas, 1996; Karl et al. 1996) - both sited in oligotrophic environments - have made seasonal to interannual observations of shallow carbon flux during monthly to bi-weekly cruises. HOTS results generally confirm the Martin et al. relationship to 500 m with pooled results over three years giving a power of 0.818 (Karl et al. 1996). BATS data do not extend deeper than 300 m but also follow Eq. 1 when averaged over several years. No break down on flux variability is available by season at either site. Other flux data from the upper 1500 m do show lack of agreement with the Martin function during some seasons (e.g. Figure 3; and review by Bishop, 1989).

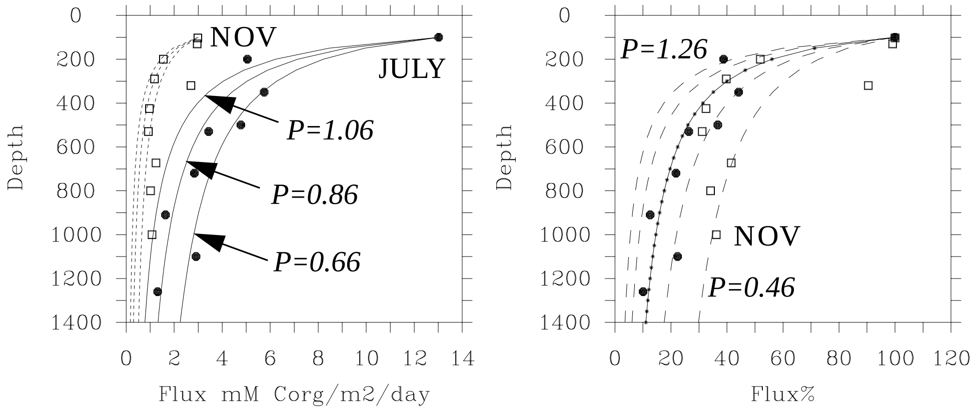

Figure 3. Flux profiles from the eastern equatorial Pacific vs. the Martin et al. (1987) model. Curves are from Eq. 1 with power changed from *0.46* to *1.26* in steps of 0.2. Data from Bishop et al. (1987). Left: flux profile data. Right: fluxes normalized to 100 m values.

Particle flux through 100 m varied by a factor of 4, but less than a factor of two by 1000 m for the two seasons sampled. The higher productivity July profile fits the Martin function well to 1300m, November data shows flux decreasing with depth but with values significantly above of the predictions of the Martin function in waters below 400m. This is better illustrated in the right panel of the figure, where flux data normalized to 100 m values. Thus, in spite of a very geographically limited calibration data set, the pre-JGOFS Martin et al. function is the 'state of the art' and applied in OGCM's as invariant in time or space. No function is available to describe the fate of settling carbonate (PIC) particles in the watercolumn.

A simple ocean carbon storage model. To predict how ocean carbon storage would change as a result of change of remineralization length scale (e.g. a fertilization or climate induced change in biological pump efficiency) it is critical to understand how remineralization varies in space and time. To illustrate this, a simple model of a hypothetical 0 to 1000 m deep water column was constructed. The loss of stored carbon is determined by the ventilation age distribution which varies from 10 years (near 100 m) to 500 years (near 1000m). Calculations investigated the impact of small changes in remineralization length scale (Figure 4). (NB this model is not intended to be correct in all oceanographic details).

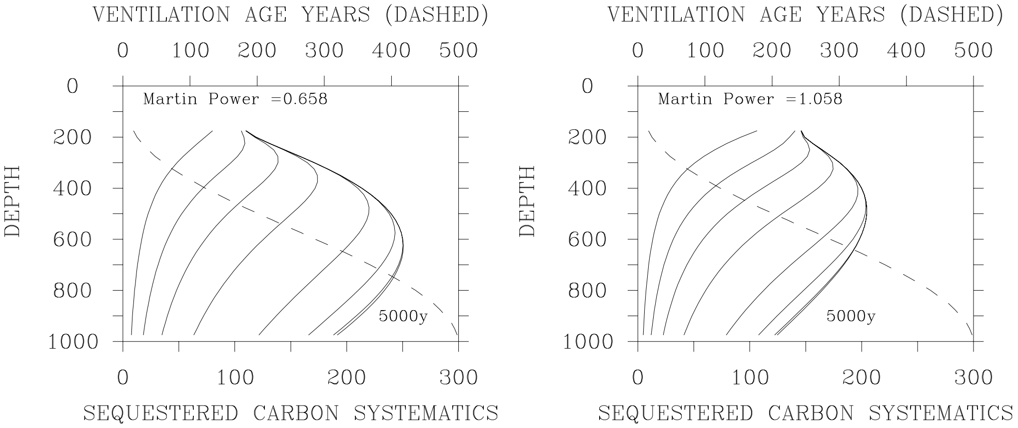

Figure 4. Sequestered carbon as a function of time (after 20, 50, 100, 200, 500, 1000, 2000, and 5000 y) for two different powers of the Martin et al. function. Not as much carbon can build up in deep waters in the case of stronger shallow remineralization (power=1.058).

The model was run over 5000 y with carbon remineralized (added to the deep water) from sinking particles based on the depth derivative of a Martin-like carbon flux profile. We chose powers of 1.06 and 0.66. Output from the simple model of relative concentrations of sequestered carbon is shown at 20, 50, 100, 200, 500, 1000, 2000, and 5000 y intervals. Clearly, the amount of carbon sequestered in the deeper water column is sensitively determined by the shape of upper water remineralization profile in relationship to the probability of ventilation as a function of depth.

A central hypothesis for OCTET is:

> ***Particle flux and remineralization scales vary with oceanic circulation and biological regimes, and that the particle flux and remineralization scales in biologically dynamics waters (outside of the warm water environments used to calibrate the Martin et al. (1997) relationship) are significantly different from the commonly-used Martin et al. parameterization.***

2 Evaluating Ocean Fertilization as a Carbon Sequestration Option

The viability of ocean fertilization as an ocean carbon sequestration option is dependent on the requirement to understand the impacts of large scale fertilization on the marine ecosystem and ocean biogeochemical cycles. A major unanswered question is:

What are the effects of long-term fertilization on carbon export and remineralization?

Recent experiments in the nutrient rich equatorial Pacific (IRONEX I, Martin et al., (1994); IRONEX II, Coale et al. (1996) and Southern Ocean (Southern Ocean Iron RElease Experiment; SOIREE, Boyd et al., (1999); Figure 5) have demonstrated how easy it is to stimulate ocean productivity through iron fertilization of nutrient rich waters. Simply stated, adding one molecule of iron to an iron limited system permits the photosynthetic fixation of ~10^5 molecules of carbon (Martin and Fitzwater 1988, Martin et al., 1992). Understanding of the after effects of fertilization is a harder problem due to the high cost and effort required for ship studies.

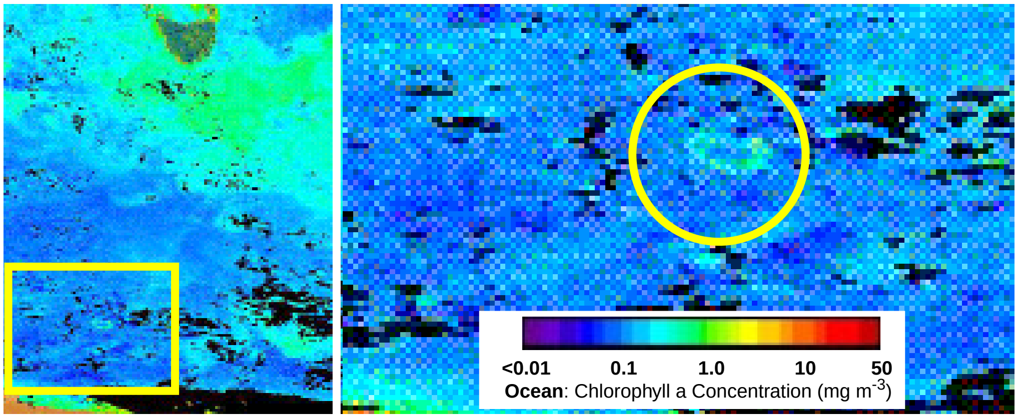

Figure 5. Monthly SeaWiFS composite image of surface chlorophyll for March 1999 showing the southern ocean from southern Australia to Antarctica and the SOIREE study area. The fertilization experiment resulted in a ring shaped enhanced chlorophyll structure (at the right) which extended over one degree of longitude when observed in SeaWiFS imagery on March 23 1999, 4 weeks after the completion of iron addition. Due to persistently cloudy conditions, data from March 23 dominated the monthly composite image in the area of the experiment. The ring structure was believed to the consequence of entrainment of the fertilized patch at the periphery of an eddy.

SOIREE results. Boyd et al. (1999) added 3800 kg of Fe (as $FeSO_4$) to a 50 km^2 area of the southern ocean near 61 S 141 E from 10 to 23 Feb. 1999. The 50-60 m deep surface layer at the onset of the experiment had dissolved NO_3, PO_4, and Si concentrations of 25, 1.5 and 9 µM, respectively. By the time the ship left the area on February 28, the patch had elongated to 150 km^2 and chlorophyll had increased 6 fold and air-sea delta pCO_2 decreased by 30 µatm compared with surrounding waters (Watson et al., submitted). The fate of the sequestered carbon was not determined.

Contrary to expectations, there was no measurable increase in particulate organic matter export (measured by the ^{234}Th deficit method) from the patch during the 18 day period of observation (Charrette and Buesseler; 1999). This lead Bakker et al (1999) to conclude that all the organic matter formed was retained in surface waters. Not only was the patch persistent 4 weeks after the experiment (Figure 5), but SOIREE scientists believe they identified the fertilized area in satellite imagery 7 weeks after the ship departed the area. This clearly was contrary to expectations that the ocean would return to its ‘natural’ state by mid-March 1999 (NIWA press release 1999).

> *There is an urgent need to develop the means to autonomously monitor biomass and flux variability to follow after effects of such experiments. The upcoming European (CARUSO) and US (SoFex) experiments in the southern ocean are planned with similar scope as SOIREE and would clearly derive benefit from autonomous observations. Future larger-scale experiments will require such observations.*

3. Strategies for assessment of carbon dynamics in the forbidden zone.

It is possible develop a prototype autonomous optical carbon flux monitoring device to address the lack of upper water column carbon flux measurements. We have already begun work in the area of autonomous particulate carbon concentration measurement under NOPP funding (Figure 6).

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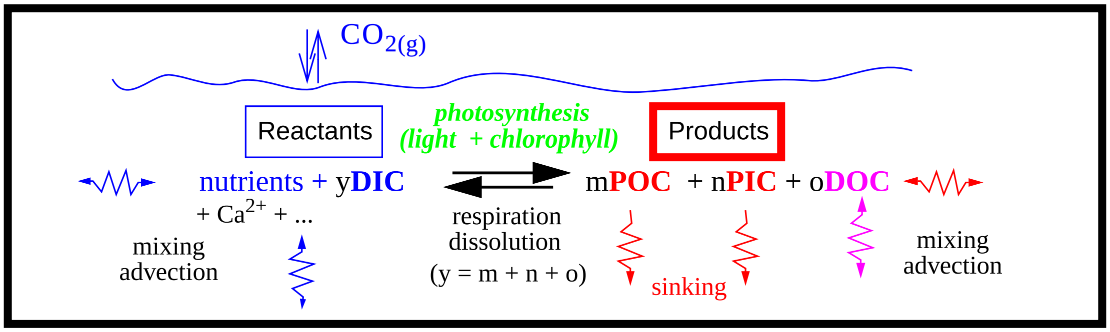

Figure 6. Simplified representation of the biological transformations of the carbon system components in seawater. NOPP funding at LBNL is supporting the development of **POC** and **PIC** **concentration** sensors. It is possible to develop optical strategies for assessment of the variability of the **POC** and **PIC** **flux**. Both developments permit integration of two basic biogeochemical measurements on floats, gliders and other autonomous platforms now available to oceanography.

Our efforts, funded under the National Oceanographic Partnership Program (NOPP) are to develop simple optical sensors for particulate organic carbon (**POC**) and particulate inorganic carbon (**PIC**) concentrations in sea water and to integrate the sensors with the Sounding Oceanographic Lagrangian Observer (**SOLO**; Davis et al. 1999; Figure 7), a low-cost (~$15k) low-power profiling float. The integrated **SOLO/carbon** platform promises the rapid and precise determination of two major products of photosynthesis: **POC** and **PIC** and physical data (T and S) relevant to the understanding of the variability of these products. A longer term goal for the **SOLO/carbon** instrument is the ability to monitor both reactants and products of photosynthesis.

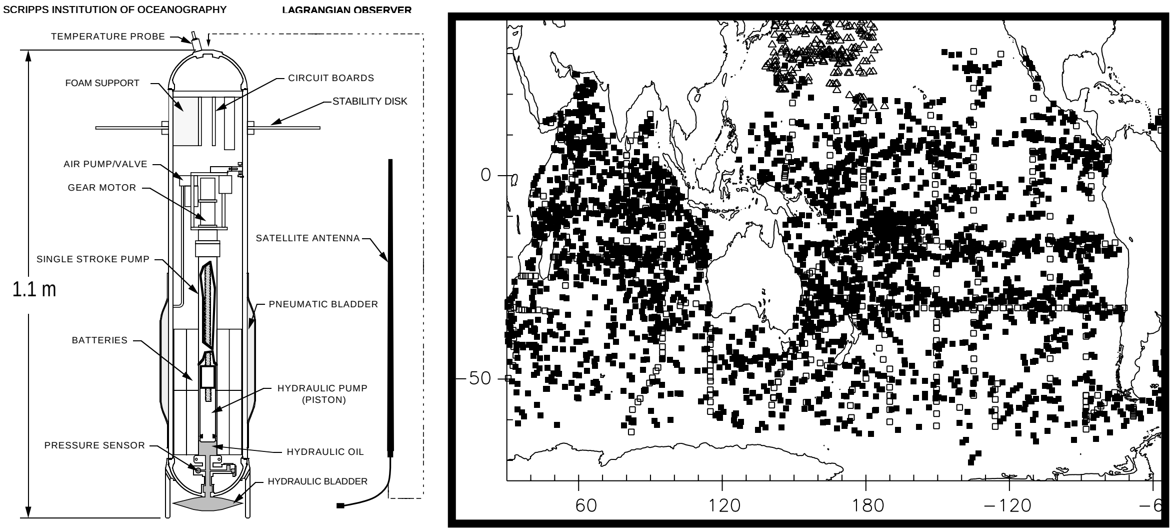

Figure 7. Left, engineering schematic of SOLO (Davis et al., 1999). Right: Partial map depicting operations of 800 profiling lagrangian floats (like SOLO) by the international physical oceanographic community. Open symbols: deployment locations. Closed symbols: a 200 day record. During operation each float drifts at mid depth (ca. 1500 m) for 10 days, profiles to the surface for location, transmits profile data (T and S) via satellite telemetry, and then returns to depth. SOLO operates by changing its buoyancy relative to surrounding water and has power to make 100 plus round trips to the surface and is designed to operate for several years. Minature submarine gliders powered by buoyancy change (e.g. the Owens/ Davis glider “Spray”) have the ability to perform of the order of 1000 round trips and navigate at 20 cm/ sec and thus have tremendous staying power in the marine environment.

Program Argo and related opportunities

Over 800 floats like SOLO have been successfully deployed to date as part of ocean physics programs (Figure 7). Based on that success, an international program named “Argo” is beginning to deploy 3000 more lagrangian profiling floats for ocean climate studies (Wilson, 2000).

> ***Octet should not miss the opportunity to add significant biogeochemical value to the Argo style floats (and gliders) by adding sensors for both POC and PIC <u>concentration</u> and <u>flux</u>.***

Remote in-situ sensing of POC and PIC. The optical detection of POC is based on Bishop (1999) and Bishop et al. (1999) who showed a robust relationship between beam attenuation coefficient, ***c*,** at 660 nm measured by transmissometer and POC measured in samples collected using the Multiple Unit Large Volume in-situ Filtration System (MULVFS).

Results show that the two properties are highly correlated (r^2 >=0.95), with practically the same relationship (within a few percent) over the wide range of ocean regions sampled; Figure 8). Therefore the calibration of ***c*** vs. POC may be largely independent of depth, ocean, and season. These results robustly reinforce the conclusions of a growing number of investigators (e.g. Gardner et al. (1993), Marra (1995), Loisel and Morel (1998), and Gundersen et al., (1998)) that POC and ***c*** are correlated.

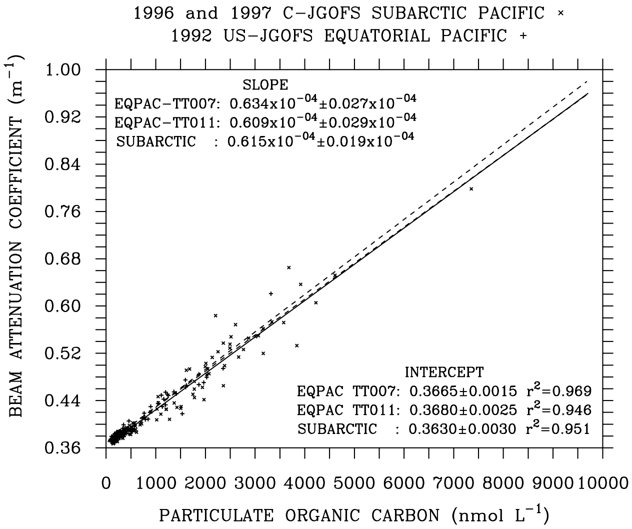

Figure 8. Comparison of POC determined from MULVFS samples vs. simultaneously measured beam attenuation coefficient, ***c***. The two dashed lines are the least squares fit to data from two 2600 km NS transects at 140W in the equatorial Pacific. The solid line fits seasonal sampling along EW “line P” at 50N between the continental margin and ocean station PAPA (50N 145W).

A PIC sensor is now under development at LBNL (Guay and Bishop, in preparation). Proof-of-concept experiments using off the shelf components have shown a fast (e.g. like a transmissometer) highly linear response (e.g. r^2 values = 0.995) to calcite concentration in the beam over the entire oceanic concentration range. The preliminary results show that the signal is not interfered with significantly by other particles. More work needs to be done, but the technique offers great promise for understanding carbonate particle dynamics (See Balch - rationale)

The prospects for *SOLO/carbon-flux floats.* The concept of a neutrally buoyant float as a platform for sediment trap measurements of carbon flux in the upper ocean was recently demonstrated by Buesseler et al. (2000). The assembly of float and trap, called a Neutrally Buoyant Sediment Trap (NBST), appears to alleviate the sometimes substantial biases in the measurement of particulate carbon flux in upper ocean waters caused by current shear (Gardner, 2000) and swimmers (Michaels et al., 1990). The trap is attached to a lagrangian drifter (like SOLO) and maintained at constant depth during sample collection. One could also modifiy a glider for this purpose.

Comparisons using surface tethered and NBST traps deployed at the same depth showed factor of two differences in the C fluxes, Th fluxes, and C/Th ratios of particles collected. NBST deployments also showed a major decrease (by a factor of 20) in the level of contamination of trapped material by swimming organisms. Although based on a small suite of analyses, Buesseler et al. (2000) open the possibility that the BATS flux data (from surface tethered traps) may be 2.5 times too low. If this is true, then the carbon budget at BATS would no longer be out of balance (Michaels et al., 1994).

Asper (1986) made the first optical characterization of particles arriving in a sediment trap moored in deep water in the Panama Basin but little similar work on his concept has taken place since. He recorded on film images of particles arriving in the trap illuminated under reflected light over a 24 hour period. His results proved the feasibility of imaging techniques for gaining information on particle flux variability.

It is feasible to marry the concepts of NBST and underwater imaging to permit time series of particle flux to be obtained autonomously and thus enable optical quantification of carbon (PIC and POC) flux and concentration as significant value added products of autonomous environmental measurements as part of physical programs like Argo. Significant work is required to calibrate and develop instrumentation capable of optical quantification of carbon fluxes; however the scientific pay back is huge.

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Variations in Fe (and other limiting trace element) fluxes to the ocean

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[Note: to be brief, I confine my comments below specifically to iron, but it should be understood that all biologically-essential and limiting chemical factors should be included.]

(1) Suggest a strategy for narrowing the uncertainties in its measurement.

Sampling contamination problems and inter-method reliability problems are rife for iron. A forthcoming measurement intercomparison organized by Hein de Baar will begin to address this question, but it is likely that a follow-up addressed at low-level Fe in Southern Ocean surface waters will be necessary. And the issue of reliable sample collection intercomparison has not been addressed. So a key part of OCTET studies on the role of Fe as a limiting nutrient will require:

(a) Completion of an analytical method intercomparison that will allow laboratories to evaluate their skills at iron concentrations typical of both surface and deep waters; this analytical intercomparison must also address concerns that different methods for iron measurement may tap different pools of iron. This intercomparison may also require some effort at intercomparing different methods for the speciation of iron and its division into dissolved, colloidal, and particulate fractions.

and

(b) Reliable methods for sampling iron in the ocean, capable of providing a global scale view of iron in the ocean, must be established and intercompared.

Sampling iron reliably may be even more of a problem than establishing a reliable analytical method. Even the best known of the trace metal laboratories obtain some samples that are contaminated and must be rejected from data interpretation. We need to test the various methods of obtaining iron samples at sea, and determine if some methods can be more reliably carried out by a broader array of laboratories. OCTET should also consider a significant sampling device development effort, whereby rapid-operation sampling devices that are simply and reliably deployed by non-experts can be developed. Given such a sampling device, we could obtain a global scale view of iron in the ocean without requiring a trace-metal dedicated global sampling program.

(c) We need to develop unattended sampling and sensor systems that can go on moorings and ships of opportunity to increase our spatial and temporal understanding iron. OCTET should direct some effort towards technology development in this area.

(2) Where geographically are these processes or fluxes most significant?

Sarmiento et al. have pointed out that a global-warming induced slowdown in thermohaline circulation may lead to increased nutrient utilization efficiency at high latitudes and hence segregate carbon from out of the atmosphere/mixed layer system into the deep sea. However, this result depends on the assumption that productivity in high latitudes will remain constant despite the circulation slowdown. Recently Andy Watson has pointed out that given the newly reported low Antarctic Fe levels and assuming a reasonable Fe:C ratio, production is limited by the Fe concentration of the upwelled waters (because upwelling Fe dominates atmospheric Fe supply in those regions). Under that scenario, production would DECREASE if the thermohaline overturning decreased, nutrient utilization efficiency would remain constant, and carbon would NOT be injected from the atmosphere/mixed layer into the deep sea. So from this perspective, research on Fe in the Antarctic is highly significant.

If there are attempts at Fe fertilization by private individuals (despite the council of scientists against these schemes), they are more likely to take place in the equatorial and high latitude North Pacific than they are in the Southern Ocean. Hence from the perspective of providing society with an understanding of the consequences of these attempts, research on Fe in these regions is also significant.

(3) Over what spatial and temporal scales must measurements be made?

First, the lack of a clear global perspective on iron variability in the ocean requires top to bottom profiles of iron for each of the major sub-basins of the world ocean, at the very least. Under the most minimalist of scenarios, this goal requires at least 20 stations in areas for which no data exists. A more complete approach would include sections along major thermohaline flow paths and hence something closer to 50-100 new Fe profiles. Many of these will can be done on ships-of-opportunity with the provision of just a few days of ship time, but a few dedicated cruises to key locations (particularly in areas where sections are appropriate) should be included under the OCTET umbrella.

Second, Fe inputs in some regions to be pulsed by dust storms, typical of the duration of weather system (a few days to a week, recurring on the same time scale. How much iron is immediately released from these pulsed inputs? How much may be released later before the mineral particles are completely removed from the euphotic zone? To what extent do these pulses affect the biota, and what is the consequence of climate-change induced changes in the intensity and frequency of these pulses? How spatially variable is Fe deposition, and how does this variability interact with the spatial scale of mesoscale eddies and biological patchiness? What happens to the biota in the seasons when the dust flux is minimal? All of these questions require information on Fe variability the scale of days through seasons to years.

Third, in some near-coastal environments, Fe inputs from the continental margins are pulsed by eddies and jets. The same questions asked in the previous paragraph can be asked in these environments as well.

(4) How would you scale measurements of these processes or fluxes to regional or global scales?

Scaling of the effect of atmospheric fluxes and their variability to regional and global scales would have to be achieved by combining process understanding with coupled atmosphere/ocean dust/sediment/circulation models. The physical models are being developed for other purposes, so this effort requires the incorporation of developing knowledge of the chemical oceanography and marine aquatic chemistry of iron into these physical models.

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University of Georgia

- Inclusion of an ocean margins initiative

The focus on offshore, particularly blue water, in the initiatives presently under discussion is too narrow. Any comprehensive program to study marine carbon flux must devote a sizable fraction of its effort to the coastal margins. Their importance is several-fold. First, the higher biological and chemical activity in these regions makes their importance much greater than their geographic size would suggest; quantitatively these regions are the most important sites for global carbon burial. Second, their proximity to the continents makes them especially vulnerable to non-steady state perturbations by human activity. Third, they are the conduit for material and energy flux to the open ocean such that neither system should be viewed in isolation from the other. Fourth, they are important sources of greenhouse gases.

Accordingly, I strongly support the inclusion of ocean margin environments within the OCTET science plan. One promising site for study is South Atlantic Bight (SAB). This region has been studied in the past (DOE Ocean Margins) and so there is baseline data that could be used guide future research programs. In the SAB, spatial coverage should extend from the coast out beyond the shelf break and should be coordinated with parallel cruises within the North Atlantic gyre. At a minimum, temporal coverage should be seasonal. Ongoing synthesis and modeling programs could be continued and expanded to scale experimental data to regional and global scales.

- Dissolved organic matter (DOM) cycling

Though the DOM pool has received renewed attention from the oceanographic community in recent years, it is still not unusual to see box models of marine microbial food webs or marine nitrogen cycles which do not include dissolved organic nitrogen (DON), and data sets which illustrate how dissolved organic carbon (DOC) and DON flux rates are related are practically non-existent. The situation is even worse with regards to our knowledge of dissolved organic phosphorus (DOP) cycling.

For example, Karl et al. (1997, 1998) have documented an accumulation of carbon-rich DOM (C:N of ~20) that is greater than the build up of particulate organic matter at station ALOHA in the Pacific. They hypothesize that the accumulation of this material indicates a decoupling of production and uptake processes. Williams (1995) reports a similar accumulation of carbon-rich organic matter in a number of very different environments. Thingstad et al. (1997) speculate that that the predominance of carbon-rich DOM is indicative of a malfunctioning microbial loop. The questions these researchers raise are provocative. At present, however, they are largely approached from the carbon-centered viewpoint which dominates biological and chemical oceanography. Accumulations of carbon-rich organic matter could be the result of changes in the carbon cycle. However, you can't fix carbon without nitrogen and changes in C:N ratios may also be due to variations in the balance of nitrogen which is released as DON versus packaged into particles. Bronk and Ward (1999) found that a significant fraction of nitrogen uptake, particularly nitrate uptake, was released as DON and not retained in the particulate nitrogen pool. How DOP fits in to these scenarios is still largely unknown. The development of more comprehensive data sets of coupled DON and DOP and DOC fluxes is essential for understanding their biochemical and biogeochemical roles in the ocean.

Strategies for narrowing the uncertainties

The lack of information on DON and DOP is largely due to the considerable methodological challenges in quantifying DON and DOP flux. Accordingly, research initiatives in this area will require considerable methodological development. I offer the following research questions with specific recommendations below each question as a way of starting a discussion.

1.0 What are the stoichiometric ratios (C:N:P) of DOM transported to the coast via rivers, produced abiotically within the coastal zone and open ocean (i.e. photochemical production), and released from autotrophs and heterotrophs in coastal and oceanic environments (via direct exudation, grazing, viral infection, etc.)?

As a starting point, the issue of filtration and filtration artifacts must be addressed from two angles. First, the process of filtration has been implicated in causing breakage of cells and subsequent organic matter release. Researchers have been arguing over this issue for 30 years and its time we focused on obtaining an unequivocal answer. Second, the more recent controversy in large discrepancies between particulate matter collection via small volume filtration or large volume remote pumps must also be addressed.

- *What is the chemical nature of the material produced?*

Researchers have focused on the very small fraction of the pool that can be isolated via ultrafiltration. A concerted effort will be needed to develop the new technologies that will allow isolation of the lower molecular fraction which comprises the bulk of the DOM pool. Special emphasis should be given to the organic fractions containing nitrogen and/or phosphorus as the nutritive value of these substrates will likely exceed the higher C:N and C:P moieties.

1) *What is the fate of the carbon, nitrogen, and phosphorus components of the DOM pool?*

Processes of interest include abiotic adsorption, autotrophic and heterotrophic uptake, photochemical breakdown. In particular the question of autrophic versus heterotrophic use of DOM needs to be addressed because it can have important implications on the time scales of retention of the material in the surface ocean and the degree that the associated carbon is lost via respiration or transported below the photic zone.

Geographically these processes are likely significant everywhere. As a starting point, the north Atlantic (BATS) and north Pacific (HOTS) stations would be good choices because of the substantial datasets already available on inorganic and organic nutrient concentration and/or flux.

The link to autotrophy argues for diel coverage of these processes. Modeling could be used to scale measurements of these processes or fluxes to regional or global scales.

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Diatoms and the Biological Pump

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Adapted from Brzezinski et al. 1997 and an NSF proposal by Brzezinski, Barber, Hutchins, Luther, Nelson, and Dugdale

Of all the potentially limiting nutrients in the ocean, only Si selects specifically against one type of phytoplankton when it becomes limiting. Diatoms have an absolute Si requirement for growth (Lewin 1962) and other marine autotrophs do not, with the result that Si limitation affects only the diatoms. Diatoms are easy to recognize visually, and their ecological importance was appreciated from an early date (*e.g.* Bigelow 1926, Guillard & Kilham 1978). Malone (1980) calculated that cells retained by nets with 10 – 20 µm mesh (a fraction usually dominated by diatoms) are responsible for only about 12% of the global-scale primary productivity of the oceans. But the biogeochemical importance of large phytoplankton became apparent when Michaels and Silver (1988) reported that those cells are the main source of carbon export in the open sea.

Diatoms are a major source of the organic matter exported from marine surface waters, and of the organic matter delivered to upper trophic levels as food. The latter fact has been recognized for decades: In 1926 Henry Bigelow paraphrased Walt Whitman's famous idea that "All flesh is grass", writing that "All fish is diatoms." During the ensuing years many studies of phytoplankton ecology and physiology focused on the diatoms. (See, for example, the review by Guillard & Kilham 1978.) But during the late 1970s and the 1980s improved methods of identifying and counting very small cells resulted in spectacular discoveries of smaller and smaller autotrophic organisms, present in huge numerical abundances in the sea (*e.g.* Waterbury *et al.* 1979, Chisholm *et al.* 1988). Interest in diatoms and Si went through a period of relative neglect, due to the emerging understanding of the ecological importance of those very small, nonsiliceous forms.

Interest in diatoms and Si cycling was rekindled when sediment-trap data revealed the vertical fluxes of biogenic particulate matter in the deep sea. Sediment-trap records from a variety of ocean habitats showed strong temporal correlation between the downward fluxes of particulate organic carbon (POC) and diatom opal, implying that diatoms are the autotrophic source of much of the sinking POC (*e.g.* Honjo *et al.* 1995, Nelson *et al.* 1996, Scharek *et al.* 1999). The importance of diatoms to carbon export has been confirmed by ^{234}Th-based export studies in a variety of marine habitats (Buesseler 1998). An unexpected result of these observations is that diatoms contribute significantly to flux even in areas where they are not dominate the plankton (Brzezinski & Nelson 1995, Scharek et al. 1999). Globally, the diatoms' contribution to export appears to be greater than their contribution to total primary productivity for several reasons, including their tendency to dominate the phytoplankton during times of high productivity, to form large, rapidly sinking aggregates and to be a preferred food source for meso- and macrozooplankton, which are large enough to migrate vertically and whose fecal pellets sink rapidly (Nelson *et al.* 1996).

The importance of diatoms to the biogeochemistry of the open sea elevates the significance of silicic acid as a key nutrient regulating biogeochemical cycling in offshore waters. The availability of dissolved Si has been shown to control diatom silica production rates, at least at times, in every natural system examined to date (Nelson et al. 1976, Nelson & Brzezinski 1984, Nelson & Tréguer 1992, Brzezinski & Nelson 1996, Nelson & Dortch 1996). Limitation of diatom metabolism by the supply rate of silicic acid results in a physiological cascade that affects their primary productivity and nitrogen use (Dugdale et al. 1981), potentially altering regional nitrogen and carbon cycling. For example, the supply rate of silicate to diatoms has been hypothesized to control the level of primary productivity and new production in the Equatorial Pacific (Ku et al. 1995, Dugdale & Wilkerson 1998).

Empirical evidence from several recent field programs confirms that diatoms are important to new and export production in several oceanic habitats. Diatoms had a major role in both new and export production during the JGOFS process studies in the North Atlantic and the Equatorial Pacific. Diatoms dominated the vernal bloom in the JGOFS North Atlantic Bloom experiment leading to the depletion of silicic acid before nitrate (Sieracki et al. 1993). The consequent limitation by Si may have lead to the rapid export of the bloom to depth (Sieracki et al. 1993). Similar rapid export of large cells has been observed in the Equatorial Pacific where large flocs of relatively fresh phytoplankton, mainly large diatoms, were observed covering an extensive area of the sea floor at depths >4000 m (Smith et al. 1996). Time-series sediment traps studies in the same region show that pulses of POC and biogenic silica export occur simultaneously implying an important role for diatoms in carbon flux (Honjo et al. 1995).

Diatoms have also been shown to be important to new and export production at both US JGOFS time-series sites. The flux of POC at the Hawaii Ocean Time-series (HOT) site displays a distinct summer maximum coincident with the annual maximum in the flux of diatom silica (Scharek et al., 1998b). Studies of silica production and export in the Sargasso Sea indicate that diatoms, while rare in the surface waters, account for 13 - 26 % of annual primary production and 16 - 40 % of annual new production (Brzezinski & Nelson 1995, Brzezinski & Kosman 1996, Nelson & Brzezinski 1997). A similar result was obtained in the western equatorial Pacific by Blain et al. (1997) who estimated that diatoms account for a third of primary productivity in that region.

Dugdale and colleagues mathematically explored the consequences of Si limitation in an ocean where diatoms dominate new production (Dugdale *et al.* 1995). They referred to the resulting control mechanism as a "silicate pump", whose net result is to make Si the main regulator of new production in surface waters where nitrate is reasonably abundant. By that hypothesis silicic acid ($Si(OH)_4$) is selectively removed from surface waters because of its low regeneration rate, while nitrate remains plentiful because ammonium and urea are regenerated rapidly in surface waters and are readily available to the phytoplankton. This results in Si limitation of diatom productivity, and hence in Si regulation of organic-matter export. Dugdale *et al.* identified those areas in the ocean where the silicate pump appears to be most likely to operate. They noted that several so-called High Nutrient Low Chlorophyll (HNLC) areas have very low ratios of [$Si(OH)_4$] to [NO_3^-], causing Si to regulate of new production by limiting diatom growth and productivity. Those areas, which Dugdale *et al.* termed low-Si HNLC areas, are (1) the eastern equatorial Pacific, (2) the region offshore of Peru to the Galápagos Islands, (3) the upwelling area off northwest Africa and (4) the circumpolar band in the Southern Ocean between the Polar Front and the Subantarctic Front.

There are very large gaps in our understanding of the role of Si as a regulator of diatom productivity and new production. In large part this is due to the small size of the global data set on diatom silica production. At last tally only 280 profiles of silica production rates and < 50 profiles of silica dissolution rates have been obtained (Nelson et al., 1995) leaving large gaps in our understanding of the global silica cycle in all areas of the ocean. The Ross and Weddell Seas of the Southern Ocean are best understood, but studies in the Antarctic Circumpolar Waters, the mid-ocean gyres number less than six. Even in coastal waters where diatoms are more abundant only a handful of studies have been conducted outside of the major upwelling zones. Further expansion of the data set should allow a more refined understanding of the regulation of the biological carbon pump by Si.

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Narrowing critical uncertainties in the ocean carbon cycle:*The Biological Pump*

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"The biological pump separates physical oceanography from biogeochemistry"

Introduction

OCTET seeks to advance our understanding of the ocean carbon sink. As stated in the OCTET Prospectus, there are essentially two ways for the ocean to influence the transfer of CO_2, namely through the solubility pump and the biological pump. We have made considerable progress in quantifying the magnitude of the solubility pump through direct measurement and modeling. I think the is because the solubility pump lends itself well to modeling (temperature vs. solubility is known; wind speed vs. transfer velocity can be predicted; ocean models of physical transport exist) and measurement (there are now accurate and precise data sets on the delta CO_2 between the air/sea).

I would argue that the biological pump is much less well constrained. Studies of C flux between the base of the euphotic zone and depth are limited precisely because we are lacking in measurements and models appropriate to this depth region. If any atom of C that exchanges between the terrestrial, atmosphere and ocean reservoirs is to be considered "lost" to the ocean sink on time scales relevant to climate change, than we must take on the challenge of quantifying the flux of C into the mid and deep ocean. While on large time and space scales upwelling and export must balance, changes in the export efficiency and relative ratio of export (C vs. N, etc) can impact the ocean C sink.

Comments on the biological pump

- Export fluxes can be measured directly (sediment traps) & indirectly (radionuclides; delta stocks, particle abundances/sinking rates)
- Export controls include:
    - Physical- particle abundances; stickiness/quality; resuspension (margins);
    - Biological- food-web control; mid-water processing; microbial
    - Chemical- remineralization (chemical- calcite/aragonite); adsorption/desorption
- Ratios of organic to inorganic carbon, N, P, Si, Fe, etc. and *changes* in these ratios are important.
- Mid water biological communities and vertical migration are poorly sampled & understood
- The biological pumps is often parameterized as constant with depth, season, location (e.g. Martin *et al*.) and if there is likely considerable variability in this relationship

We are poised with the onset of OCTET to make considerable progress in this area as promising new technologies and measurement strategies can be envisioned, including:

- Better direct and indirect particle collectors & counters
    - Neutrally buoyant traps; autonomous particle counters; optical sensors
- Better methods to quantify stocks
    - Moored chemical sensors (O_2; nutrients, ^{234}Th)
- Mid-water observatories
    - AUV, ROV, submersible technologies

- Chemical analyses continue to improve to tell us about particle sources (organic biomarkers; stable isotopes), ages (^{14}C; radionuclides) & fluxes (radionuclides & budgets)

Proposed strategies and study areas
Focus studies on regions with large biological control on C flux- including:
N. Atlantic, N. Pacific & S. Ocean (e.g. see Takahashi OCTET statement)

Depths:
Focus attention below winter mixed layer to depths around 1000m
why? steepest gradient in particle flux.
and/or emphasis on those waters not labeled with bomb tritium (i.e. define ocean sink by C that reaches depths that are not ventilated on time scales <decade).

Time and space scales:

- Biological pump is by definition seasonal
- Spatial scales of sinking particles can be parameterized (function of sinking speed and depth, i.e. Siegel *et al*.) & will range from 10 km^2 for upper 100m (sinking rates 10-100m/day) to ≈100's km^2 (more appropriate to upper 1000m).
- Scaling to regional and large global scales will require a better understanding of the rates and controls on export and remineralization. Perhaps it is premature to promise that these can be scaled using models or satellite color, or other global scale techniques.

Priorities within OCTET & studies of the biological pump

This document was written to serve as one discussion point within OCTET. It was written from my perspective/bias studying particle dynamics. Obviously, OCTET will need to prioritize within the program what scientific goals are most worthwhile. My reason for picking the biological pump is that I feel we understand its controls and magnitude much less well than the solubility pump. If the biological pump is not as significant for the global C sink, then it might not be high priority, but this need not be an "either-or" situation.

Within the biological pump, studies on the rates and controls on export and remineralization are important. Models which incorporate these controls should be encouraged. Euphotic zone biogeochemistry and physics are important in the context of their impact the quantity and quality of sinking particles and/or the relative rates of POC/DOC export. Sedimentary processes are important if they can be linked to current export processes and as they provide past records of the biological pump (*but* you need to understand remineralization and redistribution within sediments to interpret records- not always an easy task!).

Francisco Chavez

MBARI

After reading the OCTET prospectus I felt the following issues might be further discussed at the meeting.

The first, and one that defines the sampling strategy to a first order, relates to the importance of low latitude nutrient supply relative to the high latitudes. If as the geochemists have argued the low latitudes are at steady state on time scales of years then their impact on atmospheric carbon dioxide concentrations is neglible on the climate change time scale. If this is true then a primary focus for OCTET should be the Southern Ocean since it dominates the high latitude regions where unused surface nutrients are currently subducted before being consumed by biological processes. However, if this steady-state premise is violated then the focus of OCTET should be reconsidered. In a relatively obscure publication (Chavez and Barber, 1985) I calculated that if removal of carbon from the upper ocean happened at a 7.5:1 C:N ratio (based on sediment trap analysis, higher if one considered dissolved material) while supply was occurring at the Redfield ratio of 6.6:1 then the Eppley and Peterson (1979) estimate of new production drove a net export of carbon of 0.5 gigatons per year. Most estimates of new production are well in excess of the Eppley and Peterson value resulting in an even greater sequestration potential. Furthermore, one estimate of global new production (Chavez and Toggweiler, 1995) suggests that on the order of 75% is occurring at low latitudes. Are there other mechanisms at work that would make the low latitude ocean an important player for atmospheric carbon dioxide concentration on the climate change scale?

Secondly I support the need for “constraining the spatial and temporal patterns of surface CO_2 concentrations and fluxes in the North Atlantic and North Pacific Oceans on seasonal and interannual timescales.” There is potential for significant scientific payoff and it would be a program of reasonable size and scope for OCTET. It includes high latitudes, subtropical gyres and coastal and equatorial margins. What will be required for air-sea fluxes is a sampling program that will allow for the construction of Takahashi et al.-like maps of air-sea flux over seasonal to interannual scales. My strategy would be to use the lowest cost surface drifter possible by concentrating on only those measurements that are absolutely required (delta pCO2, salinity perhaps). From current observations one can calculate the required density of drifters needed to construct statistically significant surface fields of the North Atlantic and Pacific. Not only would this sampling program constrain the air-sea flux variability but we would certainly gain many new insights into the processes governing air-sea flux much like satellites opened our eyes to variability in SST, chlorophyll, sea level etc. Once drifters are made more sophisticated (profiling, more instrumentation etc.) then achieving the desired spatial sampling might become prohibitively expensive. Discussion at the meeting might focus on other sampling/platform alternatives that would result in achieving the desired resolution and also on what is the desired resolution.

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Eppley and Peterson (1979) everyone knows that one.

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I guess the process that interests me most is the possibility of a "reverse biological pump." The idea comes from a number of recent reports that suggest, based on biological incubation data, large regions of the ocean may be net heterotrophic. The data for the N. Atlantic are especially good; the data for the Arabian sea suggest this is also the case. That is, rather than being a net assimilator of CO2 and producer of O2, the biological component actually is a net assimilator of O2 and producer of CO2. This reverse biological pump does not necessarily imply that a region of the ocean (including physics and chemistry) is a net source of CO2; the total net source/sink strength depends on the rate at which atmospheric CO2 is rising in comparison to the rate at which biology produces more CO2 than it consumes.

The best way to get at this, I believe, is to couple the biological measurements with better physical approaches to gas flux. Oxygen is much easier to handle in the ocean for a number of reasons than is pCO2. The mass spec approaches of B. Luz and S. Emerson, coupled with high quality measurements of O2/Ar ratios are a very powerful tool, especially when coupled with traditionally bottle incubations measurement of GPP and R.

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I. Physics: A basic process in ocean physics that is important for understanding the carbon cycle, that may be altered by global change, is the variability of the ventilation rate of ocean waters with carbon dioxide. Decade timescale variations were observed in the water mass renewal rate of the Sargasso Sea from 1953-1979 [1]. Similar variability extended back to A.D. 1885 [2]. Deser and Blackmon [3] found variability of the winter SST anomaly east of Newfoundland which covaried with the water mass renewal rate. In the N Pacific, decadal variability of the climate mean state shifted abruptly in the N Pacific Ocean in 1976. Also, more frequent, severe El Niño events occurred after this time. The reasons given for this decadal-scale shift have varied from global warming [4], to natural variability caused by interactions between circulation in the tropical and extratropical Pacific [5]. Were there similar changes earlier this century, or before? How has the presence of excess carbon dioxide and other radiatively important gases in the earth system affected the natural variability?

A reliable strategy for narrowing the uncertainties in the measurement of non-steady state behavior in ocean ventilation on greater than interannual time scales is to reconstruct climate records for the late Holocene in the surface and subsurface ocean using multiple tracers in annually banded recorders (i.e., varved sediments, sclerosponges, corals). Cadmium/calcium ratios in seasonal coral and sclerosponge bands may reveal past nutrient levels in surrounding surface and subsurface waters, respectively. Strontium/calcium ratios in these corals (and perhaps sclerosponges) can yield SST, and subtraction of the SST signal from coral $\delta^{18}O$ (which is a function of SST and salinity) can reveal records of past salinity. As increased ventilation is usually accompanied by additional mixing with cooler subsurface waters, measurement of $^{14}C/^{12}C$ ratios (which usually decrease with depth in the water column) in the corals would help to constrain the relative changes in vertical and horizontal mixing over time. This ratio ($^{14}C/^{12}C$) also records the uptake of fossil fuel derived CO_2 by the oceans (included in the Suess Effect). Cadmium/calcium, ^{230}Th and ^{14}C in deep corals have also been used successfully to reconstruct century time-scale changes in ventilation rates of intermediate and deep water masses [6].

Areas of special importance for discerning ventilation variability are higher latitudes where seasonal mixing occurs to several hundred meters depth. However, since changes occur in the penetration of temperate waters through the subtropics and into the tropics, including the tropics in these studies is necessary. Measurements should be made in most major current regimes of the temperate and tropical Atlantic, Pacific and Indian Oceans (6-10 sites per ocean). Some tropical and subtropical records are already available from sediments, sclerosponges and corals in the Pacific and Atlantic/Caribbean and some show interannual, decadal and/or centennial variability in water masses near the surface.

II. Biogeochemistry. Whether or not the transport of organic carbon from the surface to the deep ocean, or that from the coastal regions to the interior of the ocean basin will change in the future is unknown. These questions can be investigated using concentration and isotope ($\delta^{13}C$ and bomb ^{14}C) signatures of the various organic carbon pools. Few ^{14}C profiles are available largely because of: a) the difficulty of collecting clean samples that are large enough to analyze, and b) the expense of radiocarbon measurements. Because bomb ^{14}C was introduced to the atmosphere in the late 1950s and early 1960s, any carbon pool that contains post-bomb levels contains carbon that was produced in surface waters or on land during the last few decades. Separating the organic matter from the colloidal and particulate pools into its various organic fractions for analysis will help to understand which components of the carbon are ‘younger’ or ‘older’ with respect to turnover in the ocean.

Several profiles of the concentrations and isotopic measurements (^{14}C and $\delta^{13}C$) in a given ocean basin (i.e., N Pacific or N Atlantic) are needed to narrow the uncertainties in the transport of carbon from the surface to the deep ocean, and from the coastal regions to the interior of the ocean. These profiles would need to be repeated 4 - 5 times during the next 15 - 20 years to determine any significant changes. To achieve this level of measurement, one would need to make AMS measurements of ^{14}C as easily obtainable as $\delta^{13}C$ measurements presently are using light isotope ratio mass spectrometry. New AMS instruments are now available that would allow a small to intermediate group of investigators to attain the thousands of measurements per year needed for a project of this magnitude.

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Narrowing critical uncertainties in the ocean carbon cycle: *Ecosystem Processes in the mesopelagic diagenesis layer.*

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> *"One who breaks a thing to understand it, departs the path of wisdom" ---- Gandalf*

Introduction

JGOFS saw many developments, advances and innovations in ocean science. Some were technical, some theoretical, and some sociological. All led to new discoveries. Among the key sociological developments mentioned by several people at the US JGOFS get-together in San Antonio, was the remarkable way physicists, numerical modelers, biologists and chemists learned to work together as JGOFS matured. I think a key feature of OCTET will be a fuller realization of this aspect of the JGOFS heritage. Although many will currently label OCTET as the "chemical" member of the new trio of oceans programs, and EDOCC the biological element, I want to argue here that OCTET needs – cannot do without – a strongly integrated series of in-depth ecosystem studies. In addition, we need a major new effort aimed at the zone of the ocean directly underneath the euphotic zone (ca 100-1000 m) where most organic matter diagenesis occurs.

Coordination with EDOCC may fulfill some of these needs, yet how the two programs will evolve, coalesce, interact and cooperate remains to be seen. EDOCC, as presently configured, carries a strong emphasis on molecular, genetic and physiological approaches to studying upper ocean biology. One useful division which might allow the two programs to maintain focus and use resources efficiently, would be for EDOCC to work up to the organismal level of organization, while OCTET concentrates on community- and ecosystem level studies. Union of these two approaches is ultimately necessary and should be sought, but it will take longer than the next few years to accomplish this goal. For example, the newest generation of large scale, coupled 3D ocean models now incorporate rudimentary but explicit ocean biology (e.g., P-Z-N-D models), but conceptual shortcomings as well as hardware constraints still prevent formulating global models with details of individual species interactions now being revealed by molecular approaches. Modelers and geochemists will need strong input on ecosystem processes for mechanistic understanding of chemical fluxes and incorporating the understanding in new models.

Needs and Approaches

The JGOFS Core Measurements defined a minimal suite of biological phenomena to be addressed in the process studies and time series. This suite included a limited number of biomass components and biological process observations, initially defined by the then-current modeling capability (e.g., Fasham-type models). OCTET needs to build on the JGOFS synthesis and redefine a new suite of ecosystem-level processes to comprise its core program. Like JGOFS, OCTET will not be able to study every aspect of ocean ecology, so it must concentrate on resolving key processes in the biological pump, especially those which might respond most sensitively to climate change. As before we will need to focus on key processes in strategically-chosen areas or regimes in which they can be studied best.

Three topics seem especially critical:

- Processes governing particle export and sinking rates
- Processes controlling DOC production, consumption and export
- Processes causing switches between N, P and Fe limitation, and changes in Redfield ratios

I would like to come out of OCTET/EDOCC with the capability to predict, within better than a factor of two, particle and DOC export fluxes, and the partitioning between these two modes of export, as a function of region and season, so we can begin to build up a more complete partitioning of the ocean into meaningful biogeochemical regimes. Longhurst et al's partitioning of the ocean into ecological provinces based on remotely sensed chlorophyll and circulation provides a wonderful foundation for this work, but it still remains to put pertinent carbon flux patterns and storage mechanisms into the picture.

What processes do we need to emphasize? I think JGOFS did an outstanding job of measuring new and regenerated, as well as total primary production, and rates of herbivory, especially by microzooplankton. But the key measurements needed to relate primary production directly to POC and DOC export were mostly lacking. Size-fractionated primary and new production, DOC production by phytoplankton and grazers, nutrient limitation of DOC oxidation, particle aggregation and sinking, and predation of microzooplankton by meso- and macrozooplankton (a dominant but neglected term in particle fluxes) all need better coverage.

Finally, one large region is still *mare incognitum.* The ocean interior, especially the depth zone from ca 100 – 1000 m where most particle and DOC diagenesis occurs (recall the Martin curve), needs vastly improved attention if we are to attain a better predictive insight into ocean carbon flux. This layer is the filter through which organic matter enters to deep ocean carbon reservoir. To lend a biogeochemical identity to this zone, I call it the *mesopelagic diagenesis layer*. JGOFS has documented rates of particle flux through this layer, but in most cases neglected any mechanistic study below the euphotic zone. This zone presents special logistic and conceptual challenges for us to overcome. It may be dominated by bacterial or animal metabolism but we don't know which, or how they vary. The "bacterial" assemblage might in fact be dominated by the *Archaea*, a major kind of life about which we know almost nothing (they are not *Bacteria*, and are as different from bacteria as either group is from us!). Respiration and nutrient regeneration are the critical processes in the mesopelagic; however they proceed at rates near the limits of detection. A major new improvement in technology is needed to improve the sensitivity of analytical approaches for work below the surface layer. Because we know so little about the biological processes driving particle and DOC flux and breakdown in the mesopelagic diagenesis layer, we have little insight into the space and time scales characterizing variability there. For example, we recognize generally that there are different oceanic biomes or ecosystems analogous to terrestrial grasslands, forests, etc., but this recognition is drawn mostly from our knowledge of the surface layer. What is the vertical extent of recognizable ocean biome characteristics? Is the mesopelagic diagenesis layer under the central gyres distinct from that under the HNLC regions or the subpolar bloom provinces? Gaining the ability to provide answers to these questions would be a major advance in marine ecology, and is critically needed for a better understanding of ocean carbon flux.

I think a major attack on the mesopelagic diagenesis layer should be a central part of OCTET.

The net annual carbon and oxygen flux from the subtropical South Pacific Ocean: A natural test of the iron hypothesis

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An accurate estimate of the annual organic matter export from the surface ocean-- the biological pump -- requires time-series measurements, and in this regard, the ocean is still dramatically undersampled. Oxygen mass balances at the three comprehensive ocean time series stations --the subtropical Atlantic near Bermuda (Jenkins and Goldman, 1985; Spitzer and Jenkins, 1989); the subarctic Pacific at Station P (Emerson et al., 1991), and the subtropical Pacific at Station ALOHA (Emerson et al., 1995; Emerson et al., 1997)--are compared with other methods of estimating organic carbon export at these locations in Table 1. At Station ALOHA the values determined by O_2 mass balance are within the uncertainties (±50%) of those measured by organic carbon fluxes, and carbon isotope mass balances (Emerson et al., 1997). At Station P the mean annual organic carbon export rate from oxygen mass balance is about 40% lower than that determined from recent annual measurements of ^{14}C productivity and ^{15}N uptake (Harrison et al., 1999; Varela and Harrison,1999), which is also likely within the uncertainties of these determinations. This type of closure has not been achieved at Bermuda where the oxygen mass-balance estimates continue to be about a factor of two greater than that determined from organic matter mass balances (Carlson et al., 1994). The O_2 estimates have been corroborated by mass balances of nitrate and calculations of the oxygen utilization rate beneath the euphotic zone (Jenkins and Wallace, 1992) suggesting that these values are correct.

The organic matter export measured from the subtropical north Pacific and Atlantic is about the same as that in the subarctic Pacific and about half that estimated in the Equatorial Ocean (Figure 1). This perspective on the biological pump magnitude and oceanic distribution does not agree with export estimates by either satellite color measurements (Falkowski et al., 1998) or ocean GCMs (Six and Maier-Reimer, 1996). Both of the latter suggest much greater organic matter export in areas with high nutrients in the surface waters than in the subtropics. Nutrient sources for the relatively large carbon export from the subtropics implied by the measurements in Table 1 is a major problem. There is growing evidence that nitrogen fixation supplies a large fraction of the necessary nitrogen (Michaels et al., 1996; Karl, 1997; Gruber and Sarmiento, 1997). It is known that nitrogen fixing organisms require iron, and it has been hypothesized that this is the reason for present levels of nitrogen fixation in the North Pacific and Atlantic Oceans (Falkowski et al., 1998). If this is the case then one would expect lower levels of export production in the area of the ocean which receives the least atmospheric iron, has very low surface nutrients and where iron is believed to be limiting--the south Pacific subtropical gyre

(Duce and Tindale, 1991; Behrenfeld and Kolber, 1999). To my knowledge there are no annual estimates of carbon production in this area, and very few measurements of export production. Estimates of seasonal net outgasing of oxygen using the global data bases (Najjar and Keeling, 2000) suggests that oxygen production in the south Pacific Ocean is, if anything, greater than that in the north Pacific, calling into question the importance of iron limitation to export production.

I propose that a program be developed within OCTET to determine the magnitude of the biological pump in the south Pacific Ocean and investigate the mechanisms of nutrient supply. This requires a time series of measurements over a period of several years. Critical measurements are those necessary to achieve an oxygen and carbon isotope mass balance in the upper ocean (Emerson et al., 1997). The lion's share of the time series work would be done using remote vehicles capable of profiling at a single location and determining T, S, and oxygen concentration. There are several versions currently available and being tested to do this type of work. The time-series station should be visited four times per year to service the vehicles and obtain discrete samples that cannot be measured remotely (δ^{13}C-DIC; O_2/Ar/N_2; particle fluxes; primary production and new production). We should explore the possibility of collaborating with French oceanographers, who have an oceanographic presence and experience in this part of the world's ocean.

Table 1. The net annual C production determined by oxygen mass balance and other methods at the 3 long-term ocean time-series stations and the equatorial Pacific. Oxygen production estimates were converted to carbon production using a $\Delta O_2/\Delta C$ of 1.5.

Location	Net O_2 production	Other Methods
	(moles C m^{-2} yr^{-1})	
Subtropical Pacific (HOT)[a]	2.7 ± 1.7	1.6 ± 0.9,2.0 ± 1.0
Subarctic Pacific (Stn. P)[b]	2.0 ± 1.1	2.8 ± ?
Subtropical Atlantic (Bermuda)[c]	3.3 ± 1.1	1.8 ± 1.0
Equatorial Divergence[d]		4.2 ± 2.3

(a) Emerson et al. (1997). The values for "Other Methods" are from DIC - δ^{13}C mass balances, and organic C fluxes.
(b) The "Net O_2 Production" number (Emerson et al., 1991) assumes carbon export in the winter is half that in summer. The value from "Other Methods" is calculated from ^{14}C primary production and ^{15}N f-ratio measurements (Boyd and Harrison, 1999; Varela and Harrison, 1999).
(c) O_2 mass balance (Spitzer and Jenkins, 1989). The value for "Other Methods" is based on particulate C and DOC fluxes at the Bermuda time-series station (Carlson et al., 1994).
(d) Based on δ^{13}C-DIC and DIC mass balance (Zhang and Quay, 1997). Assumes fall equatorial Pacific conditions are representative of annual non-ENSO period.

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The Role of the Oceans on the Interannual Variability of Atmospheric CO_2

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The U.S. Carbon Cycle Science Plan (CCSP) focuses on two fundamental scientific questions: "What has happened to the carbon dioxide that has already been emitted by human activities (past anthropogenic CO_2)?" and "What will be the future atmospheric CO_2 concentration trajectory resulting from both past and future emissions?" It is the latter question that holds the largest scientific and societal interest. Because carbon reservoirs in the ocean, atmosphere and terrestrial biosphere are irrevocably linked, the CCSP calls for an integrated approach to studying the carbon cycle, focusing on elucidating the key unknowns in the system. The ocean plays a critical role in the global carbon cycle since it has a vast reservoir of CO_2 containing approximately 50 times more CO_2 than the atmosphere and therefore exerts a controlling influence on atmospheric levels. It rapidly exchanges CO_2 with the atmosphere, with exchange times of approximately 8 years (where the exchange time is defined as the atmospheric reservoir size of about 750 PgC divided by the gross air-sea flux of about 90 PgC yr-1). It also takes up a substantial portion of the anthropogenically-released CO_2. The oceanic component of an observing system for the global carbon cycle must serve two functions. First, it should measure the magnitude, spatial distribution, and the interannual to decadal variability of carbon uptake patterns in the global ocean. Second, it should provide a framework for which studies are implemented to improve our mechanistic understanding of processes controlling regional uptake. Both these components are critical to provide the data necessary for improving model projections of future atmospheric CO_2 concentrations.

A major question concerning the ocean carbon cycle is how much does the ocean uptake of CO_2 vary from year to year, or, in other words, how constant are the processes that control the uptake currently and in the future? Atmospheric inverse methods utilizing atmospheric CO2, O2/N2 and 13C/12C [*Bender et al.*, 1996; *Keeling et al.*, 1998; *Francey et al.*, 1995; *Keeling et al.*, 1995; *Rayner et al.*, 1999] have given provocative, but not completely consistent, results suggesting interannual oceanic variability of up to 3 PgCyr-1 (This is demonstrated in a figure in *Le Quéré et al*. (in press) showing a time series of the interannual sea-to-air flux of CO2 as estimated using ocean observations and models and using atmospheric observations and models.) To date, indirect oceanic and oceanic model results suggest that the interannual variability is much smaller than initial atmospheric inversions suggest [*Lee et al.*, 1998; *Le Quéré et al,* in press; Loukos et al., in press]. For example, the recent GCM model results of *Le Quéré et al* [in press] suggest that the global variability of CO_2 in the oceans from 1979 through 1997 averaged about ±0.4 PgCyr-1, with approximately 70% of the variability originating from the Equatorial Pacific (Fig. 1). Our oceanic measurements to date suggest that ENSO related interannual variability in the Equatorial Pacific is at most 0.7 PgCyr-1 [*Feely et al.*, 1999*; Chavez et al.*, *1999*; Table 1]. The key question that must be addressed in this regard is: are we missing a large part of the oceanic variability in our ocean based models and observations, or are there shortcoming and biases in the atmospheric estimates? There is evidence from satellite-based temperature and chlorophyll data in other equatorial and subtropical regions which suggest additional ENSO-related interannual variability of CO_2, but we have insufficient observational pCO_2 data in these regions to determine yearly changes in extratropical CO_2 uptake. The lack of observational data at appropriate temporal and spatial resolution has prevented a conclusive determination of this variability on a global scale.

One hypothesis for extratropical investigations is that the CO_2 anomaly associated with large-scale ocean-atmosphere reorientations, like the ENSO phenomenon, will propagate into subtropical and subarctic waters of the Pacific and will be modulated by the Pacific Decadal Oscillation (PDO). In the Atlantic Ocean, the North Atlantic Oscillation (NAO) is believed to affect surface water CO_2 fluxes. The resulting changes in SST and associated changes in biogeochemical processes by the NAO, PDO, and extratropical ENSO manifestations could lead to large interannual variations in the CO2 sink. The North Atlantic is the largest CO_2 sink per unit area, taking up 0.5-1 $PgCyr^{-1}$. Interannual changes in pCO_2 in this region could thus significantly influence the global flux.

One important need is to gain a better understanding of the spatial patterns of surface ocean CO_2 concentrations and their variability. Seasonal and interannual variability of CO_2 concentrations in the surface ocean are one to two orders of magnitude greater than their annual increase due to uptake of anthropogenic carbon (e.g., Bates et al. 1996, Winn et al. 1994; Feely et al., 1999). In addition, the seasonal and interannual variability in CO_2 concentration gives information on how the carbon cycle functions, and can be used in conjunction with other methods to help understand regional and global patterns of carbon uptake. A very promising development of the last decade to improve spatial and temporal coverage is new instrumentation that will make it possible to measure CO_2 (DeGrandpre et al. 1995, Friederich et al. 1995, Goyet et al. 1992, Merlivat and Brault, 1995) and other properties autonomously from moorings, drifters and volunteer observing ships (VOS). An expanded network of long-term ship of opportunity, time-series, and drifter measurements, emphasizing acquisition of data for representative ensembles of oceanic regions and conditions, is required to define by observation the spatial distribution and temporal variability of pCO_2 and air-sea flux. To understand the processes controlling pCO_2 additional variables to be measured might include: dissolved inorganic carbon (DIC), temperature, salinity, nutrients, oxygen, and related tracers. These high-frequency measurement programs at basin scale over both the Pacific and Atlantic will provide an estimate the magnitude of oceanic sources and sinks of CO_2 from independent methods such as pCO_2 data, atmospheric measurements of CO_2, O_2/N_2 and 13C/12C, and surface water 13C measurements. This will provide tools and data necessary for constraining estimates of the terrestrial carbon sinks from improved inverse models.

Table 1. Comparison of Estimates of CO_2 Sea-to-Air Flux from the Equatorial Pacific

Region of Interest	Year of Study	Area x 10^6 km^2	Mean ΔpCO_2 µatm	Annual Flux PgC	Reference
Non-El Niño Conditions					
5°S, 5°N, 100°W, 170°E	1979-80	11	70	0.6	Keeling & Revelle (1985)
10°S, 10°N, 80°W, 150°E	1979-80	31	51	0.8	Smethie *et al.* (1985)
10°S, 10°N, 80°W, 135°E	1984	35	60	0.6	Feely *et al.* (1987)
10°S, 10°N, 80°W, 120°E	1984	39	60	0.8	Volk (1989)
10°S, 10°N, 170°W, 180°	1989	35*	50	0.96	Wong *et al.* (1993)
5.5°S, 5.5°N, 80.5°W, 134.5°E	1989	21	79	0.4	Inoue & Sugimura (1992)
10°S, 10°N, 80°W, 135°E	1996	35	63	0.9±0.6	Feely *et al. (1999)*
El Niño Conditions					
10°S, 10°N, 80°W, 135°E	1983	35	2	0.02	Feely *et al.* (1987)
10°S, 10°N, 170°W, 180°	1987	35*	5	0.09	Wong *et al.* (1993)
5.5°S, 5.5°N, 80.5°W, 134.5°E	1987	21	31	0.4	Inoue & Sugimura(1992)
10°S, 10°N, 80°W, 135°E	1992	35	27	0.3±0.2	Feely *et al.* (1995)
10°S, 10°N, 80°W, 135°E	1993	35	51	0.6±0.4	Feely *et al.* (1999)
10°S, 10°N, 80°W, 135°E	1994	35	60	0.7±0.4	Feely *et al.* (1999)
10°S, 10°N, 80°W, 135°E	1997	35	31	0.4±0.2	Feely et al., submitted
10°S, 10°N, 80°W, 135°E	1998	35	30	0.4±0.2	Feely et al., submitted

*Extrapolated to 35 x 10^6 km^2

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The Role of Modeling in Future Carbon Cycle Studies

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Here I outline two distinct types of modeling both of which, I believe, should be pursued as part of any future carbon cycle research programs: Quantitative and qualitative models. I like to distinguish between these approaches efforts which, in my view, have quite different philosophies and approaches. I think this distinction is important and not always recognized. Below I describe the role of these two modeling approaches and make some personal recommendations as to the directions each should move as part of OCTET.

Of course, while it is useful to highlight the differences and individual values of these two modeling approaches, they are not mutually exclusive but somewhat symbiotic.

1. Quantitative Modeling

Extrapolation of data to basin/global scales using models (e.g. estimation of ocean uptake of anthropogenic CO2). The natural direction for quantitative estimation is to move more towards inverse modeling and data assimilation which provide means of careful and rigorous quantification of both the desired quantities and uncertainties. This kind of modeling generally requires the most comprehensive and realistic prognostic model of the system in order to minimize model-data misfit in a meaningful way.

This kind of modeling has parallels with numerical weather forecasting.

This type of study interfaces well with large scale data sets such as the global carbon survey type observations, but can use any and all data to improve estimation. Also may be applied on any scale, not just global.

Recommendations for OCTET:
(i) Continued effort to provide quantitative interpretations and extrapolations of present and (forthcoming) data sets using data assimilation techniques to provide a rigorous framework.
(ii) Continued effort to bring forward models to the appropriate level of description to enable best use of the data.
(iii) Interface with ongoing physical climate system efforts (e.g. CLIVAR). Leverage on products such as ocean circulation state estimates from the PO community.
(iv) We need continued OCMIP type studies to advance the global forward models for this format.

2. Qualitative Modeling (i.e. process modeling)

The other application for modeling are idealized studies with a strong qualitative emphasis, seeking better understanding of complicated/complex systems, for example temporal variability and the role of physical-biogeochemical interactions. Such models generally knowingly forgo the ability to make quantitative analyses and predictions but retain the clarity with which to reveal the underlying mechanisms and interactions.

The classic Harvardton Bear models are a good example. They have been very influential on how we think about global change and the carbon cycle. Their strength is in their simplicity and transparency, not in their numerical prediction abilities.

This type of modeling interfaces well with local process study type observations and paleo data sets, as an interpretive tool.

Recommendations for OCTET:
(i) In addition to quantitative approaches, we must strongly support process oriented models to develop our understanding of complex interactions of climate and biogeochemical systems.
(ii) Currently cutting edge question is what are feedbacks between these systems (on interannual to multi-millennial timescales and beyond).

THE BIOLOGICAL PUMP: A DOC PERSPECTIVE

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INTRODUCTION:

This document provides data and ideas to stimulate a discussion on the partitioning of the biological pump between sinking biogenic particles and dissolved organic carbon (DOC). Historically we have thought of sinking particles as the primary driver of AOU in the ocean, but it now appears that in the upper ocean much of the AOU can be driven by DOC mineralization. While POC export dominates globally (probably 90% of total AOU), there is significance to export as DOM: it can contribute to 30-50% of AOU development in the upper 500 m of the water column; it is exported at non-Redfield C:N ratios, carrying 50-100% more carbon per unit nitrogen exported; and it follows the same paths to depth as does anthropogenic CO_2. Here I present observational data demonstrating DOC export, report where DOC is exported in the ocean, and provide a hypothesis as to why some sites of ocean ventilation export DOC, while others do not.

DOC EXPORT: OBSERVATIONS

Data demonstrating the export of DOC are available from only a few sites – not because the process doesn't occur often but because of a paucity of data. In this document I show DOC export with North Atlantic Deep Water (NADW) formation, North Pacific Intermediate Water (NPIW) formation, and with ventilation of the main thermocline of the western South Pacific. Figure 1 shows the gradient in deep ocean DOC, with the highest concentration found at the site of NADW formation and the lowest concentration at the distal end of the lower limb of the great ocean conveyor belt (the northern North Pacific). There is a 29% drop in DOC concentration along the path of flow. Export of DOC with NADW formation occurs at a rate of about 32 Tg y^{-1}, supplying perhaps 50% of the organic matter required to drive AOU in the deep North Atlantic (Hansell and Carlson, 1998).

A shallower ventilation of the ocean occurs with intermediate water formation. For example, new NPIW forms east of Japan, feeding a low salinity lens of water into the North Pacific subtropical gyre at depths of 400-1000 m. Fig. 2a shows the distribution of salinity in the upper North Pacific along 152°W, with the upper and lower density boundaries for NPIW shown as bold lines (sigma theta 26.6 and 27.4). Fig. 2b shows the concentrations of DOC from 1000 m at several points along the line. In the region of strong subtropical water influence (salinity >34.4; south of 25°N) the DOC concentrations are uniform at ≈38 μM. To the north, where lower salinity, subpolar water has strong contributions, the DOC concentration is elevated by 8-9 μM. This horizontal gradient exists because newly formed NPIW is enriched with DOC at the time of formation, exporting 28 Tg C y^{-1} as DOC (Hansell et al., 2000) and driving 30% of AOU near the site of formation (Ogura 1970).

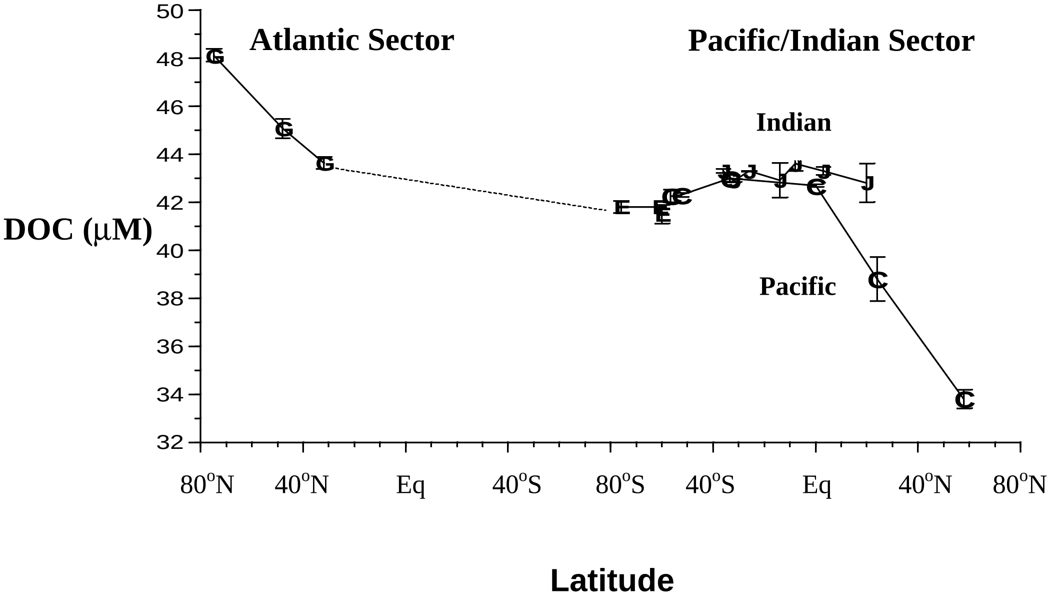


Fig. 1. Distribution of DOC in the deep ocean.

The main thermoclines of the world's oceans ventilate each winter as well. At the time of overturn, DOC enriched surface waters are entrained and subducted downward along isopycnal surfaces. A representative isopycnal surface from the western South Pacific (170°W) is that of sigma theta 26.0-26.5. A regression between DOC and AOU concentrations along that surface demonstrates that DOC contributes 30-40% to AOU development in the upper 500 m of the water column (Fig. 3). The balance of the AOU in the upper 500 m (60-70%) is due to oxidation of sinking particles. At depths >500 m along this line all of the AOU is driven by particles (Doval and Hansell, 2000).

CONTROLS ON DOC EXPORT

The data provide clear evidence for DOC export to a range of depths, from that of the main thermocline to that of deep water. One might think that all other sites of ocean ventilation would support DOC export as well, but such is not the case. DOC export with Antarctic Intermediate Water (AAIW) formation appears to be nil, as is true for Antarctic Bottom Water (AABW) formation. It appears that the Southern Ocean is unable to export DOC to any significant extent. The reason for this is that DOC concentrations in the surface waters of the Southern Ocean are very low just prior to deep mixing. The DOC that was produced over the summer periods, which can be several 10's of μM above winter values, is very labile to microbial attack and therefore mostly mineralized by the time of overturn. There is an absence of significant excess DOC in the surface water that could be exported.

The northern hemisphere also produces labile DOC, which can be eliminated before overturn as well. But what makes the waters north of the Southern Ocean different is that they carry with them a significant load of semi-refractory DOC, with turnover times of years to decades. Hansell and Carlson (in prep) hypothesize that it is this material that must be present at the time of overturn for DOC export to be a significant process. The semi-refractory fraction of the DOC pool is produced in the low to mid latitudes of both the southern and northern hemispheres, but only in the northern hemisphere is this material transported with the great western boundary currents (the Gulf Stream and the Kuroshio Current) to the high latitude sites of intermediate and deep water formation. The Antarctic Polar Front (APF) prevents a similar introduction of semi-refractory DOC, produced at lower latitudes, to the sites of AAIW and AABW formation, so DOC export there is minimal.

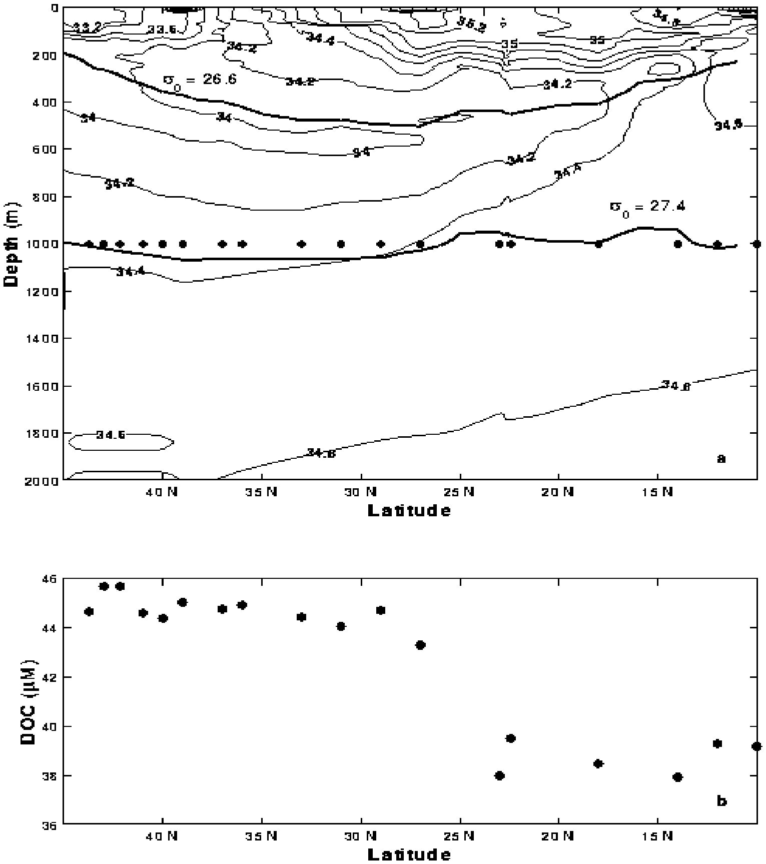


Fig.2 a) Salinity along 152°W in the North Pacific Ocean. Bold lines are upper and lower sigma theta boundaries of North Pacific Intermediate Water. 2b) Distribution of DOC along the transect at 1000 m.

The global distribution of the primary sites of ocean ventilation is shown in Fig. 4. Also shown is a line approximating the position of the APF. We hypothesize that sites of ocean ventilation located north of the APF are the primary conduits for DOC export. The sites south of the APF are very weak exporters of DOC. The significance is that POC export dominates in the Southern Ocean, but it’s contribution to total export in all other locations is a fraction, albeit a large fraction, of export.

CONCLUSIONS:

The global export of DOC likely occurs at a rate of 1-2 Pg C y^{-1}, or 10% of new production and export with the balance largely occurring as sinking biogenic particles. A difficulty slowing development of our understanding of particle export, though, is that the process can be very short lived, dispersed both spatially and temporally, and, therefore, easily missed. Direct measurements of the process are notoriously difficult to achieve. DOC export, on the other hand, appears to take place at well known locations, at well established times. The contribution of DOC mineralization to AOU development can be resolved with a good degree of certainty by tracking gradients of each along isopycnal surfaces emanating from the sites of ocean ventilation. Because the balance of the AOU development along these surfaces is due to POC mineralization, we may gather a good deal of insight on the dynamics of POC export (such as mineralization length scales, locations, etc.) by placing a new focus on DOC's contributions to export. The important sites for study are those sites of ventilation shown in Fig. 4.

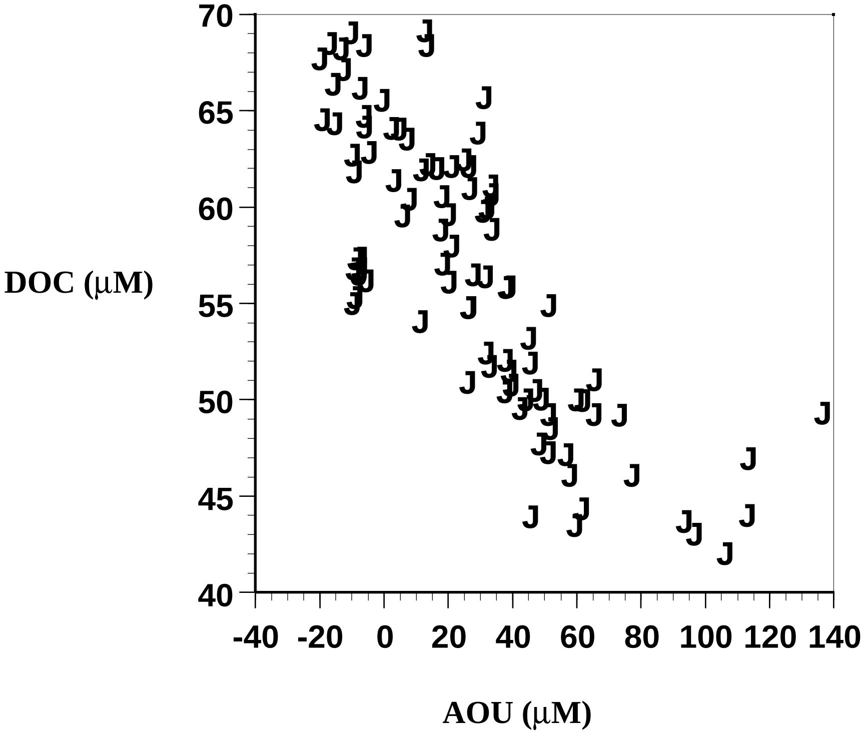
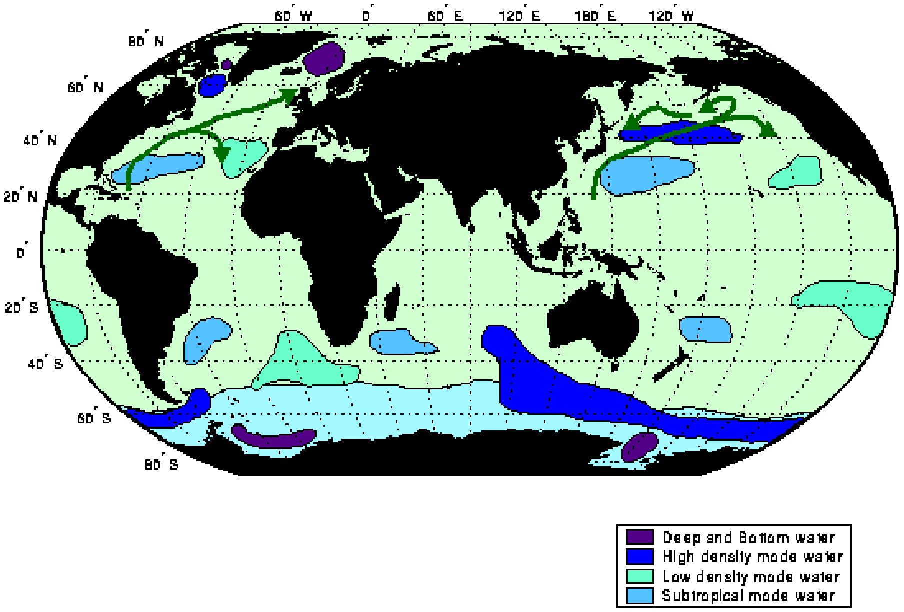


Fig. 3. DOC and AOU along sigma theta 26-26.5 in the western South Pacific Ocean (170°W).

Fig. 4. Distribution of sites of ocean ventilation (modified from Talley 2000). The line near 60°S approximates the position of the Polar Front, south of which DOC export is negligible. Arrows indicate northward transport of semi-refractory DOC.



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THE NEED FOR COASTAL/MARGIN RESEARCH WITHIN GLOBAL CARBON CYCLE STUDIES

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Estimates of the transfer of carbon from surface to deep ocean layers where exchange with the atmosphere is limited to time scales longer than a century will require a quantitative understanding of the biogenic fluxes within continental margin regions. Numerous lines of evidence demonstrate the importance of margin systems.

Compilations of benthic chamber and deep sediment trap results suggest that approximately half of the biologically-driven particle flux to the deep ocean (below the main thermocline) occurs within the continental slope and rise environments. Thus, on this vertical scale, the biological pump cannot be quantified without including fluxes along margins. The focus of future studies of the biological pump should focus on the transfer to below the main thermocline and to below the mixed layer of marine sediments because it is the transfer across these horizons that represents a long-term storage of carbon of relevance to global climate change issues.

In addition, processes along ocean margins, are known to influence water mass properties within ocean basins via lateral exchange. Examples include sedimentary denitrification, opal regeneration and iron release that may alter nutrient ratios within the water column and thereby control ecosystem composition and biogeochemical processes on basin scales.

Biologically mediated transfers of carbon are known to be variable on a wide range of temporal and spatial scales even in the open ocean. ENSO, NAO, and numerous other indicators and factors suggest that true steady state is rarely, if ever, achieved on the time scale of individual oceanographic expeditions. Repeated sampling at specific locations over time periods sufficient to reveal sustainable fluxes are required to quantify the role of the biological pump in carbon transfers. Logistically, such studies are more efficient when located near ports and other observing systems. Efficient, repeated sampling within coastal ecosystems may greatly enhance our understanding of the global biological pump.

Studies assessing the role of biological transfers in controlling climate in the coming decades will require analysis of the impacts of changing ecosystems on carbon transfers. Coastal ecosystems are being subjected to greater anthropogenic stress and the impacts of global climate change may also be concentrated in continental margin regions. It is likely, therefore, that coastal ecosystem structure will undergo greater and more rapid change than its open ocean counterparts. Due to the development of coastal observing systems and the possibility of more frequent shipboard observations from nearby port facilities, the impacts of changing conditions on ecosystem composition and biogeochemical processes will be detected earlier and may be monitored more frequently in coastal/margin studies.

Additionally, sedimentary records of carbon fluxes, surface species and chemical biomarkers are available in margin environments, occasionally with annual resolution. Present measurements can, therefore, be interpreted in the context of past and potentially changing conditions.

Ecosystems are complex and our understanding of the biogeochemical cycling within ecosystems is limited by the human resources and instrumentation and measurement technologies that can be applied to any given location. Biogeochemical studies in coastal/margin locations permit more efficient shiptime use by minimizing transit times and by allowing shorter, more flexible expeditions. This will permit participation by a greater proportion of the oceanographic research community. The added diversity of measurement techniques and intellectual perspectives should accelerate the rate at which an understanding of the marine biological pump is achieved.

For the above reasons, I believe that some portion of the OCTET research effort should be directed toward the biogeochemical cycling of carbon at the ocean margin.

What stocks of limiting nutrients exist in the ocean beyond the usual HNLC areas or N-fixation? How might they change in time?

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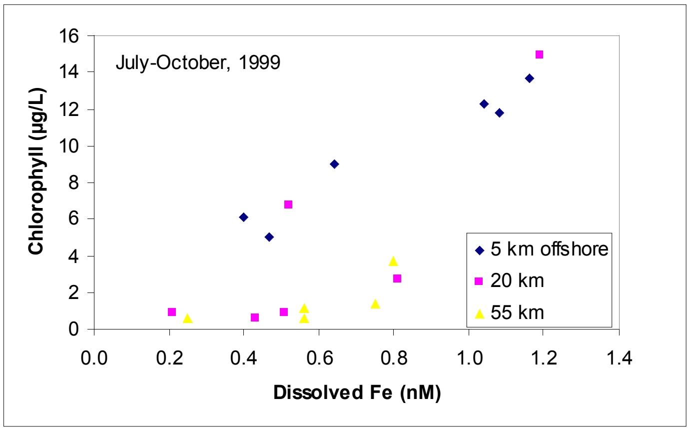
Changes in the strength of the biological carbon pump are believed to have a large effect on atmospheric carbon dioxide concentrations over glacial/interglacial cycles. Two primary mechanisms are discussed as agents to alter the amount of carbon removed from the mixed layer by phytoplankton each year. One is variable utilization of macro-nutrients in High Nitrate, Low Chlorophyll regions, generally driven by changes in the flux of the micro-nutrient iron. The second is variable rates of nitrogen fixation in oligotrophic gyres, which allows excess PO_4^{3-} in surface waters to be consumed. Again, changes in the flux of iron may play a role in regulating N-fixation.

These are not the only mechanisms by which the biological pump may be altered. I discuss two examples here, but there are surely more. Sunda and Huntsman (Nature, vol. 390, 389-392, 1997) have shown that phytoplankton growth at low light requires higher cellular iron quotas than does growth at high light.. A corollary of this would be that greater iron availability would allow phytoplankton to grow at greater depths. I.e., the euphotic zone might be extended to greater depths. If increased iron flux globally produced a 5m depth range extension into water which had 5 µM NO_3^-, then this would be approximately equivalent (5 µM * 5 m* 10-fold greater area than So. Ocn.) to the potential of the entire Southern Ocean HNLC system (20 µM * 20 m * 1 area unit) (Johnson et al., Mar. Chem. 57, 137-161, 1997). Of course, this calculation ignores differences in upwelling rates, but Si limitation may also operate in much of the Southern Ocean.



Secondly, the role of the coastal ocean as an agent of global change has been widely ignored. Work by Hutchins and Bruland (Nature, 393, 561-564, 1998) shows the potential for iron to limit phytoplankton production in coastal areas. We have undertaken a time series study of iron distributions within the MBARI Ocean Observatory in Monterey Bay (Johnson et al., Nature, 398, 697-700, 1999). Unpublished results shown in the attached figure demonstrate a strong effect of iron on biomass accumulation during summer months. Throughout this entire period, NO3- and Si are present at levels >6 µM, except in the largest blooms when macro-nutrients are depleted. These blooms only occur when iron is injected into the system. Coastal new primary production is 20% of the global total (Chavez and Toggweiler, in Upwelling in the Ocean: Modern Processes and Ancient Records, C.P. Summerhayes, et al., eds. Wiley, 1995, pp. 313-320). A doubling of new primary production in the coastal ocean, with enhanced iron input, would again equal new primary production in the modern Southern Ocean.

Paleooceanographic studies of organic carbon mass accumulation rates (or barium, opal and other paleoproduction indicators) indicate that these processes (open ocean carbon export and coastal carbon export) varied systematically over glacial-interglacial cycles. The variations in these processes are, in fact, much more clearly defined than productivity changes in the Southern Ocean (about which we are still arguing). Studies of these processes and their response to environmental perturbations may be key issues in understanding the response of the ocean to climate variability. We should not ignore them in new programs to determine the flow of carbon through the ocean.

Ecological Stoichiometry of the Ocean's Biological Pumps

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General Introduction

The large and dynamic oceanic reservoir of carbon, approximately 4×10^{19} g distributed unequally among dissolved and particulate constituents with various redox states, plays an important role in global biogeochemical cycles. The two largest pools are dissolved inorganic carbon (DIC = $[H_2CO_3] + [HCO_3^-] + [CO_3^=]$) and the less oxidized pool of mostly uncharacterized dissolved organic carbon (DOC). A chemical disequilibrium between DIC and organic matter is produced and maintained by numerous biological processes. The reversible, usually biologically-mediated interconversions between dissolved and particulate carbon pools in the sea collectively define the oceanic carbon cycle.

Primary conversion of oxidized DIC to reduced organic matter (dissolved and particulate pools) is generally restricted to the euphotic zone of the world ocean through the process of photosynthesis. The supply of reduced carbon and energy required to support subeuphotic zone metabolic processes is ultimately derived from the upper ocean and is transported down by advection and diffusion of dissolved organic matter (Toggweiler, 1989), gravitational settling of particulate matter (McCave, 1975) and by the vertical migrations of pelagic animals (Longhurst and Harrison, 1989) and phytoplankton (Villareal et al., 1993). Each of these individual processes, collectively termed the "biological pump" (Volk and Hoffert, 1985) is controlled by a distinct set of environmental factors and, therefore, the relative contribution of each process may be expected to vary with changes in habitat or with water depth for a given habitat.

When particulate export is expressed as a percentage of contemporaneous primary production, this value is termed the export ratio (Baines et al., 1994). Results from broad-scale, cross-ecosystem analyses suggest that the export ratio in oceanic habitats is a positive, non-linear function of total integrated primary production (Suess, 1980; Pace et al., 1987; Martin et al., 1987; Wassman, 1990), with values ranging from less than 10% in oligotrophic waters to greater than 50% in productive coastal regions. It should be emphasized, however, that the field data from which the existing export production models were derived are extremely limited and that open ocean habitats, in particular, are underrepresented (Baines et al., 1994). Because most global ocean primary and export production occurs in oceanic habitats (Martin et al., 1987), it is important to understand the mechanisms that control the biological pump in those locations so that we can make accurate and meaningful predictions of the response of the oceanic carbon cycle to global environmental change.

The Concept of Ecological Stoichiometry

Nutrient dynamics and their role in the variability of the stoichiometry of organic matter pools is a central aspect of biogeochemical studies. Within this broad research area, ecological stoichiometry is defined as the study of the balance of energy and multiple chemical elements and their ecological interactions (J. Elser, pers. comm.). As such, it includes the subdisciplines of environmental physiology, population dynamics, community organization, ecosystem function and global biogeochemical cycles. All known organisms contain a nearly identical suite of biomolecules with common structural and metabolic functions. This biochemical uniformitarianism serves to constrain the bulk elemental composition of life. In a seminal paper, Redfield and his colleagues (Redfield et al., 1963) summarized much of the earlier research on C, N and P stoichiometry of dissolved and particulate matter pools in the sea and combined these data sets into an important unifying concept which has served as the basis for many subsequent field and modeling studies in oceanic biogeochemistry. The so-called “Redfield, Ketchum and Richards ratio” (or simply, the Redfield ratio) of 106C:16N:1P has, over the intervening decades, achieved nearly canonical status in aquatic sciences.

Despite this perceived uniformity, it is well known that the chemical composition of living organisms can vary considerably as a function of growth rate, energy (including light) availability and ambient nutrient (including both major and trace elements) concentrations and concentration ratios (Sakshaug and Holm-Hansen, 1977; Rhee, 1978; Laws and Bannister, 1980; Tett et al., 1985). For example, under conditions of saturating light and limiting N, certain photoautotrophic organisms can store C as lipid or carbohydrate thereby increasing their C:N and C:P ratios. Likewise, if P is present in excess of cellular demands, it may be taken up and stored as polyphosphate causing a decrease in the bulk C:P and N:P ratios. Conversely, when the bioavailable N:P ratio is greater than that which is present in "average" organic matter (i.e. >16N:1P by atoms) selected groups of microorganisms can exhibit a metabolic "P-sparing" and effect net biomass production with C:P and N:P ratios significantly greater than the hypothesized Redfield ratios of 106:1 and 16:1, respectively. Based on theoretical biochemical arguments, Raven (1994) predicted that the C:N:P ratio in microorganisms is non-scalable with decreasing cell size. He concluded that the C:P ratio in small cyanobacteria should be higher than in average eukaryotic phytoplankton cells. Consequently, there does not appear to be a robust constraint on ecological C:N:P stoichiometry in the marine environment.

In most open ocean habitats, there is a continuous reflux of major nutrients that over broad time and space scales is controlled by the upward eddy diffusion of dissolved inorganic nutrients balanced by the downward flux of particulate matter (Eppley and Peterson, 1979). The remineralization of sinking particulate matter within the upper mesopelagic zone of the ocean (200-500 m) sustains these large scale nutrient cycles. In the absence of other significant allochthonous nutrient sources or sinks, these coupled delivery and removal processes control both the elemental stoichiometry of dissolved and particulate pools and, ultimately, the ability of the ocean to sequester atmospheric carbon.

Selected Biological Pumps

Longhurst (1991) has previously defined three subcomponents of the biological pump, each representing a separate set of ecological processes. The rotary pump circulates materials through the microbial food web, the Archimedian pump defines the gravitational flux of fecal pellets and aggregated materials and the reciprocating pump represents the daily bi-directional migration of animals in response to light. For open ocean ecosystems, the relative contributions of these processes are poorly known. Although the Archimedian pump is generally assumed to dominate total euphotic zone export (Martin et al., 1987; Knauer et al., 1990; Karl et al., 1992), the role of yet another component, the diffusion pump, may also be important (Toggweiler, 1989; Carlson et al., 1994). The rates at which the individual components of the biological pump operate are under the control of both physical (light, temperature, turbulence) and biological (species composition, growth rate, food web structure) controls.

Each year, the biological pump removes an estimated 7 GT C (1 GT = 10^{15} g) from the surface waters of the world ocean, a value that is equivalent to ~15% of the annual global ocean primary production (Martin et al., 1987). Microbial transformation of sinking particles in the thermocline (Taylor et al., 1986; Karl et al., 1988) that gives rise to increased C:N and C:P ratios with depth can potentially drive a net atmosphere-ocean flux of CO_2 in the subtropical Pacific (cf. Winn et al., 1994). Episodic flux "events" carry to the deep sea large amounts of "fresh" organic matter with near-Redfield elemental ratios. These events may represent the bulk of the flux reaching depths greater than 1000 m (Anderson and Sarmiento, 1994), making processes within the main thermocline also dependent upon the biological pump.

After a decade of JGOFS-related research, we now are able to recognize at least four fundamentally different biological pumps with variable ecological and biogeochemical significance:

(1) The run of the mill, "**Redfield Ratio – Dissolved/Particulate Matter Pump**" wherein the C:N:P stoichiometry of the exported materials exactly balances the C:N:P stoichiometry of the subeuphotic zone supplied materials. A characteristic of this pump is the vertical attrition of mass, which is generally modeled as a normalized power function of the form $F_z = F_{150\,m}\,(Z/150)^b$, where Z is water depth and F and $F_{150\,m}$ are fluxes at depth Z and 150 m, respectively (Martin et al., 1987; Knauer et al., 1990). In this model, the regeneration length scales of C versus N and P are critical to the carbon sequestration process (Christian et al., 1997). If there is no spatial or temporal separation between C and the export production rate limiting nutrients N and P, there can be no net carbon sequestration. This biological pump paradigm is most frequently employed in models of the ocean carbon cycle but, for reasons described below, it may be the least relevant for carbon sequestration in the sea.

(2) The "**Stochastic, Event-driven Diatom Aggregation Particulate Matter Pump**" wherein some physical or biological perturbation to the biogeochemical steady-state results in the rapid growth, aggregation and export of large chain- or aggregate-forming diatoms. A characteristic feature of these rapid growth-export events is the efficient delivery of viable biomass and fresh non-living organic matter to the deep sea floor (the so called phytodetritus pulse). Even if the stoichiometry of these exported materials conforms to the Redfield ratio, there is a net removal of carbon from the ocean's surface on time scales of a few millennia and, hence, net carbon sequestration. Although aggregation events have been reported to occur in both coastal and open ocean habitats the physical, chemical and biological controls are poorly understood. While it was once thought to be coupled to the turbulent-driven supply of new nutrients by deep mixing events of eddy-induced upwelling, it is now evident that diatoms can propagate, aggregate and sink even in stratified open ocean waters (Scharek et al., 1999; Cullen et al., 2000).

(3) The "**N_2-supported Prokaryotic Pump**" wherein microbiological fixation of N_2 temporarily relieves the ecosystem of fixed-N limitation resulting P control of new and export production. Under these new habitat conditions, there is a selection for the growth of organisms with an altered ecological stoichiometry, one which produces dissolved and particulate matter with elevated C:P ratios. Export of these non-Redfield materials provides a mechanism for the net, temporary sequestration of atmospheric carbon in the surface ocean. The time scales of this process will depend upon the stability of the climate variables that first encouraged the growth of the N_2-fixing prokaryotes, and on a continued supply of bioavailable P. The latter could, in part, be satisfied by vertically-

migrating, N_2-fixing microorganisms like *Trichodesmium* (Karl et al., 1992). Additional implications of selection for the **N_2-supported Prokaryotic Pump** are presented below.

(4) The "**Ice-assisted Pumps**" wherein the formation of annual sea-ice in high latitudes promotes the removal of dissolved and particulate matter by at least two separate mechanisms: (a) conversion of DOM to POM by the freezing process and (b) seasonal proliferation of ice algae and their associated communities. Both (a) and (b), above, appear to be very important in those habitats where sea ice forms (e.g., Southern Ocean) because both processes affect an altered ecological stoichiometry of the particulate matter that is produced. In the former process, because the C:P ratio of the DOM pool is always larger than the expected Redfield ratio, there is a very high likelihood that the POM so formed via freezing and "salting out" also has altered stoichiometry. This has been documented for the Palmer Long-Term Ecological Research (LTER) region of the Antarctic Peninsula (D. Karl, unpublished data). The growth of ice algal communities under conditions of low light flux during the winter/spring season and in ice nutrient limitation also favor high cellular C:N and high C:P ratios, in part, due to low growth rate and lipid storage. When the ice melts in late spring/early summer there is an ice-assisted export of particulate matter with a stoichiometry that is very different from the local nutrient supply; and therefore net local carbon sequestration.

Of these four separate biological pumps, only the first has been studied in any detail. Unfortunately, it is the most predictable of the four and, for many reasons, the least important for the ocean's carbon cycle. If the **N_2-supported Prokaryote Pump** is found to be important in other oceanic regimes we may need to alter our most basic dogma on nutrient biogeochemistry in the sea.

Several lines of evidence from Sta. ALOHA (22°45'N, 158°W) suggest that N_2 fixation is an important contemporary source of new nitrogen for the pelagic ecosystem of the North Pacific Ocean. These independent measurements and data syntheses include: (a) *Trichodesmium* population abundances and estimates of their potential rates of biological N_2 fixation, (b) assessment of the molar N:P stoichiometries of surface-ocean dissolved and particulate matter pools and development of a one-dimensional model to calculate N and P mass balances, (c) seasonal variations in the natural ^{15}N isotopic abundances of particulate matter exported to the deep sea and collected in bottom-moored sediment traps and (d) observations on secular changes in soluble reactive P (SRP), soluble nonreactive P (SNP) and dissolved organic N (DON) pools during the period of increased rates of N_2 fixation (Karl et al., 1997).

Although N budget estimates suggest that N_2 fixation may presently supply up to half of the N required to sustain particulate matter export from the euphotic zone, the observations from Sta. ALOHA also suggest that this relatively high percentage of N_2-supported production may represent a transient ecosystem state reflecting either oceanic variability or, perhaps, an unusual state established in response to the well-documented decade-long shift in North Pacific climate (Karl 1999). This altered view of biogeochemical dynamics in the gyre may have profound influence on how one models ecosystem processes, including the potential impacts of natural or human-induced environmental change and its relationship to carbon sequestration.

A New Source of "New" Nitrogen in the Sea: A Prospectus

Open ocean ecosystems on Earth are characterized by low concentrations of fixed, bioavailable N which would appear to make them a suitable niche for the proliferation of N_2-fixing prokaryotes. However, N_2-fixing prokaryotes also prefer environmental conditions defined by high phosphorus (P), high iron (Fe) and low oxygen (O_2); near surface open ocean habitats are chronically depleted in P and Fe and are, typically, well oxygenated (e.g., O_2 = 200-250 μM).

Historical investigations conducted in candidate tropical and subtropical habitats of the world's oceans have generally failed to support the ecological prediction of N_2-fixing microorganism dominance. Existing conceptual and mathematical models of biogeochemical cycling in the ocean, therefore, generally ignore N_2 fixation as a key metabolic process.

In their now classic treatise on nutrient dynamics in the sea, Dugdale and Goering (1967) introduced the unifying concept of "new" (i.e., nutrients imported to the local environment from surrounding regions) versus "regenerated" (i.e., nutrients that are locally remineralized) forms of nitrogen. They were careful to emphasize that there were several potential sources of new N for the euphotic zone, each of equal value but with potentially different ecological consequences. Since there were few data on N_2 fixation rates when their paper was published, importation of nitrate from below the euphotic zone was considered to provide the majority of new N in the sea.

Now, thirty years after the new production concept was introduced, there is increasing evidence that rates of oceanic N_2 fixation may have been systematically underestimated or, perhaps, have increased in relative importance over time. This new evidence comes from several independent lines of investigation. One of the most interesting and provocative modern data sets is that derived from the application of novel molecular methods to detect the presence and abundance of N_2-fixing microbes either by hybridization or amplification of nitrogenase (*nif*; the enzyme system used to reduce N_2 to ammonia) genes (Zehr et al., 1998). Application of these methods to open ocean biomes in the North Atlantic and North Pacific Oceans has revealed a spectrum of previously uncharacterized *nif* gene phylotypes. Furthermore, significant *nif* phylotype diversity is apparent both within and between open ocean ecosystems. These novel data sets, when considered in concert with other recent reports of high rates of oceanic N_2 fixation support the hypothesis that N_2 fixation is a major source of new N over vast regions of the world ocean (Michaels et al. 1996; Gruber and Sarmiento 1997; Karl et al. 1997). Dugdale and Goering (1967) were careful to warn initially that if N_2 fixation was (later) found to be a quantitatively important pathway for nutrient supply, then a revision of the new versus recycled N conceptual framework would be necessary.

I submit that the time has come for a reconsideration of the new and export production paradigms. There is much at stake in this re-assessment. First, the net rate of carbon dioxide sequestration into the interior portion of the ocean is directly controlled by the source(s) of new N. If the nitrate flux dominates, there will be no net carbon sequestration because the bidirectional mass fluxes of C and N, would be nearly in balance as predicted by the new production – export production model (Eppley and Peterson 1979). On the other hand, if N_2 fixation sustains a significant amount of new and export production in open ocean ecosystems, then net carbon dioxide will be sequestered. Furthermore, N_2 fixation in the world's oceans may be controlled by the atmospheric deposition of Fe, which itself is a variable, climate sensitive parameter. Total atmospheric dust transport is also affected by humankind, including population demographics, global economies and land use patterns. These complex natural and anthropogenic interactions, with multiple potential feedback loops, provide a mechanism for biogeochemical variability in otherwise "stable and homogeneous" biomes. In this regard, the seascape even in remote regions may be strongly influenced by the landscape, and there is no question that the latter has changed significantly over the past 250 years.

If the conceptual framework of new and regenerated production is discarded, it may take many years for it to be replaced with a new, ecumenical theory of nutrient dynamics in the sea. There is no doubt in my mind that additional, important discoveries of novel unexpected marine microorganisms and biogeochemical processes will be made as we continue to explore our planet and some of these future discoveries may also challenge existing dogmas.

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Nitrogen Fixation and Redfield Stoichiometry

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(Partially drawn from a paper with Dave Karl and Tony Knap and from our Biocomplexity Proposal to NSF)

Our current conceptual model for the cycling of carbon in the ocean assumes that reactive nitrogen, mostly nitrate, limits plant growth and that the cycling of carbon can be linked to the nitrogen cycle by the Redfield stoichiometry. This is expressed in models by a simplified version of the new production hypothesis (Dugdale and Goering, 1967) that concentrates on the dynamics of nitrate and ammonia as a reflection of new and regenerated processes respectively. The carbon cycle is then reflected as a simple multiplication of the nitrogen fluxes by 6.6 (moles/mole). This is computationally tractable and, in many cases, seems to represent the dynamics of the drawdown of a spring bloom or upwelling in highly productive areas. However, the assumption that this behavior can be abstracted globally has important and perhaps un-intended consequences for the dynamics of the ocean and how we represent them in models.

The simple assumptions of a fixed Redfield stoichiometry and a nitrate-based new production system basically imply that biological processes are largely irrelevant in the global carbon dynamics that control atmospheric CO_2. In a world that operated with these simple assumptions, all of the DIC that is required to fuel phytoplankton growth is introduced to the surface when the nutrients are upwelled or mixed into the euphotic zone. It was put their by the same remineralization processes that produced the nutrient. Since the simple N cycle has no gas exchange component, a simple carbon system that is linearly linked to nitrogen will have no net gas exchange either. Most of the global biogeochemical models of the ocean are represented by these dynamics. Thus it is not surprising that they have trouble articulating the role of biological processes in the uptake of CO_2 by the ocean. Either these simple assumptions are true and ocean biology is minimally important (in which case we can probably invest our global change effort elsewhere), or we have to study the biology of the ocean from a different perspective.

The important processes for the net role of biology in the air-sea carbon balance will be those deviations from the simple assumptions that allow for a net exchange of carbon with the atmosphere. Many of these have been described, but are not usually the focus of research. If the Redfield ratio assumption is relaxed in a non-steady state world, the carbon dynamics become more interesting. An increased C:N ratio of export compared to uptake has been described in many studies and seen at both BATS and HOT. Dissolved organic carbon and nitrogen may be even more out of Redfield balance. If this dynamic is added to the link between the simple nitrogen dynamics and the resultant carbon dynamics, there is a net transfer of carbon from the atmosphere to the deep sea on the time-scales of the ventilation of those deeper watermasses. This same dynamic can also occur if the lengthscale for the depth of remineralization of carbon is larger than that of nitrogen. On millennial time-scales, this enriched deep carbon will ultimately ventilate back to the surface, however on interannual, decadal and centennial time-scales it means that a change in the rate of biological activity (and export in particular) can have a net effect on the atmospheric carbon concentration.

The other obvious modification of these assumptions is the inclusion of a gas phase or air-sea exchange to the nitrogen cycle. This will then require a gas exchange for carbon at some appropriate stoichiometry. Nitrogen deposition and nitrogen fixation are two processes where nitrogen is introduced from the atmosphere or from a dissolved gas phase that is ultimately equilibrated with the atmosphere. On a global scale, N deposition may play a modest, but increasing role (Galloway *et al.*, 1995). We are just coming to realize that nitrogen fixation may be very important in the carbon dynamics on the interannual scales of climate variability and on the centennial to millenial scales of global change.

Oceanic N_2 fixation has recently been identified as a much more significant part of the oceanic nitrogen (N) cycle than previously thought. The global rate of nitrogen fixation is now estimated to exceed 100-150 Tg N/y and global denitrification rate estimates are even higher. The balance of these two rates may directly influence the sequestration of atmospheric CO_2 in the oceans by providing a new source of N to the upper water column. On longer time-scales, they change the total amount of nitrate in the ocean within the permissible bounds of the variability of N:P ratios in organisms. This also changes the air-sea partitioning of carbon. The prokaryotic microorganisms that convert N_2 gas to reactive N are an unique subcomponent of planktonic ecosystems and exhibit a variety of complex dynamics including the formation of microbial consortia and symbioses and, at times, massive blooms. Accumulating evidence indicates that iron (Fe) availability may be a key controlling factor for these planktonic marine diazotrophs. The primary pathway of Fe delivery to the upper oceans is through dust deposition.

Perhaps the most exciting implication of the role of diazotrophy is that N_2 fixers may be directly involved in global feedback cycles with the climate system and these feedbacks may exhibit complex dynamics on many different time-scales. The hypothesized feedback mechanisms will have the following component parts: The rate of N_2 fixation in the world's oceans can have an impact on the concentration of the greenhouse gas, carbon dioxide (CO_2), in the atmosphere on time-scales of decades (variability in surface biogeochemistry) to millennia (changes in the total NO_3^- stock from the balance of N_2 fixation and denitrification). CO_2 concentrations in the atmosphere influence the climate. The climate system, in turn, can influence the rate of N_2 fixation in the oceans by controlling the supply of Fe on dust and by influencing the stratification of the upper ocean. Humans also have a direct role in the current manifestation of this feedback cycle by their influence on dust production, through agriculture at the margins of deserts, and by our own production of CO_2 into the atmosphere. The circular nature of these influences can lead to a feedback system, particularly on longer time-scales.

The key point is that the examination of the simple nitrogen dynamics and rate processes in the upper ocean that come from the basic paradigm (new production, export) may be less important than understanding how the deviations in our assumptions affect the links between elements. One of the strongest lessons from the two time-series stations and the other JGOFS investigations is that an intensive, multi-year study of each of these systems has revealed processes that are at odds with the assumptions of the simplest versions of our basic paradigms. When we include these new processes and changed assumptions, we come up with air-sea carbon dynamics that differ from the patterns in our simple models. Biology may be more important for global processes when it breaks the rules and we have to look for these unique patterns to understand their impacts.

Assessing seasonal and interannual variability of the oceanic carbon distribution and transport

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WOCE/JGOFS has recently completed the first high-quality global survey of the oceanic carbon field providing a single snapshot of the carbon distribution at the time of the early 1990's. A key concern in the interpretation of these observations is to assess how representative any single realization is. Put another way, what are the amplitudes and time scales of the chief components of variation in the ocean carbon system? In the case of heat, another climatically relevant property observed during WOCE, we can begin to answer this question. Over the past decade repeated XBT surveys across many of the subtropical gyres of the world's oceans provide a direct measure of seasonal and interannual variability of upper ocean heat content and stratification. For example, in the North Pacific, over 27 XBT lines have been completed between California and Taiwan. The mean meridional heat transport calculated from this data is 0.77 ±0.12 PW with an interannual range of 0.3 PW [Roemmich et. al., 2000].

In the case of carbon, we have no comparable basin-scale time series to assess seasonal, interannual or interdecadel variability. In the absence of the possibility for densely repeated large-scale surveys of the ocean carbon system, an alternative approach, could be to find some transfer function to relate the variability of the carbon system to the observed variability of the upper ocean heat content, stratification and transport. Such techniques have been successfully used in the spatial domain. For example, Wallace [1995] demonstrated that multiple regression analysis has significant predictive power for describing the spatial variations of the total carbon distribution within an ocean basin. Do similar regressions/correlations hold for temporal variability? We currently do not know. Thus, an important goal of any future program to study the ocean carbon system should address this deficiency.

As with the previous observational programs, we can maximize available resources by piggy-backing any carbon observation program onto other existing and planned observational initiatives. But how best do we coordinate the goals of carbon cycle science with observational programs designed to study other aspects of the climate system, e.g. GOOS, CLIVAR? Two distinct, but not mutually exclusive, approaches to this coordination are described below. The first I refer to as ``Observational Piggy-back'' while the second is an ``Interpretational Piggy-back''.

An observational piggy-back was practiced during the WOCE/JGOFS carbon survey: carbon measurements are conducted alongside other observations. During WOCE this was possible because the hydrographic surveys were implemented from ship platforms which provided the space and water-catching ability to allow for laboratory chemical analysis. However, future observations of oceanic variability of the heat and salinity distribution will be largely gathered from autonomous platforms such as floats and mooring. The carbon community can take advantage of these platforms provided they develop and deploy low-power, long-life sensors to mount on these autonomous platforms. While efforts to develop these sensors is currently underway, large-scale deployment of these new technologies is many years away.

An interpretational piggy-back approach seeks to utilize the large data sets on ocean variability which will be gathered in the next decade. Rather than attempting to measure carbon in the complete global network, we would seek to understand how much we can learn about the variability of the carbon system by the observed variability of other, more easily measured *in situ* properties; specifically, upper ocean heat content. Upper ocean thermal structure is one of the most easily observed *in situ* features of the ocean. A historical data base of upper ocean heat content is large and will grow rapidly in the next decade. Does the variability of upper ocean heat content and transport provide a good representation of similar features of the ocean carbon system? At what time scales is there good correlation? At what time scales does this correlation break down? If there is significant correlation on interannual time scales, we can learn a great deal about the global variability of the carbon system from the currently planned programs to monitor upper ocean temperature. On the other hand, if there is not useful temporal correlation between the properties, studying these differences would lead to increased understanding of the mechanisms governing variability in the ocean carbon system.

The ``Interpretational Piggyback'' approach will still require a directed program of ocean carbon observations. However, instead of attempting a global survey, a process study focused on a limited region might be more useful. The effort would seek to measure the large-scale covariance of the ocean carbon and heat systems. This program could utilize existent technologies and methods. Examples of observations might be: 1) a transbasin hydrographic section repeated on seasonal time-scales, 2) an array of moorings which would use existing rosette technology to capture water samples for later laboratory analysis. Such an array might be deployed for several years, capturing water samples on a bi-monthly basis. Both of these methods would provide the database to begin to measure the seasonal and interannual variability of the carbon system and the covariance of upper ocean carbon and heat content. While these approaches might only be feasible for a basin-scale study, they would provide a direct means to interpret and diagnose carbon system variability in the global data sets obtained by other elements of the global observing system.

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Future Ocean Carbon Cycle Studies: The Importance of Ocean Time-Series and Mesopelagic Process Studies

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Time-Series Stations

Future ocean carbon studies, whether OCTET, EDOCC, or some combination of the two should consider conducting process studies in the context of established time series studies. Our present ocean time-series stations, BATS and HOTS, have proven to be a tremendous resource to assess seasonal and annual variability in carbon cycle processes; to conduct focused process studies; and, to test various types of biogeochemical models. Given this background of data and understanding, it is surprising that we did not conduct JGOFS-type process studies at the HOTS and BATS sites with all of the detailed measurements of trophic processes,nutrient cycling and flux measurements that were done at the JGOFS process study sites. Detailed process studies imbedded within time-series studies allow one to assess the physical, chemical and biological conditions of the study site before and after the process measurements and thus provide an essential framework for interpreting rate measurements in the context of seasonal, annual and decadal changes.

Future carbon studies in both the open ocean and on coastal margins should establish time-series stations with comparative approaches in different ecosystems. Long-term studies are essential to understand the changes that are occurring in the ocean carbon cycle. While previous expeditionary process studies have resulted in many new insights into important biogeochemical processes, these "snapshots" do not allow us to confidently extrapolate rate measurements that vary as the scalar properties of the ecosystem change. An integral component of future process studies should be the establishment of time-series stations that provide an essential context of variability of the system.

Mesopelagic Studies

JGOFS processes studies were concentrated primarily in the euphotic zone. Through these studies we have greatly increased our understanding of the food-web processes that recycle carbon within, or export carbon from the euphotic zone. Thorium and sediment trap studies have estimated the gravitational flux at different depths in the water column, however we have little notion of the mechanisms responsible for the utilization and transformation of carbon below the euphotic zone. JGOFS process studies in the Arabian Sea and Equatorial Pacific have shown that roughly 90% of the carbon fixed by autotrophs is recycled within the water column with approximately 10% exported as the gravitational flux at the base of the euphotic zone. Sediment traps at 1000 m have shown that approximately 90% of this gravitational flux from the euphotic zone is recycled between 100 and 1000 m. Thus the percentage of the carbon that is recycled (90%) is roughly the same in the euphotic zone and in the 100 to 1000 m depth horizon. Is this recycling distributed homogeneously between 100 and 1000 m ? How do the bacteria, protozoa, mesozooplankton and fish determine the rates of carbon utilization, transformation and export in the mesopelagic zone? We might guess that there are particular depth horizons that are "hot spots" for recycling, regeneration and the utilization and repackaging of sinking particles. If one compares the "average" particle concentration (POC) from bottle casts to the carbon requirements for the resident mesopelagic mesozooplankton, the plankton should all starve to death. Clearly this is not the case, implying that sinking particles may be concentrated at particular density interfaces where the mesozooplankton could not only meet their nutritional needs but also repackage sinking material into faster sinking fecal pellets. In the case of meso- and macrozooplankton , there are similar species and genera worldwide in the mesopelagic depths. Thus there are particular species that could be important in the interception and utilization of sinking carbon particles.

Monitoring Anthropogenic CO_2 in the Oceans

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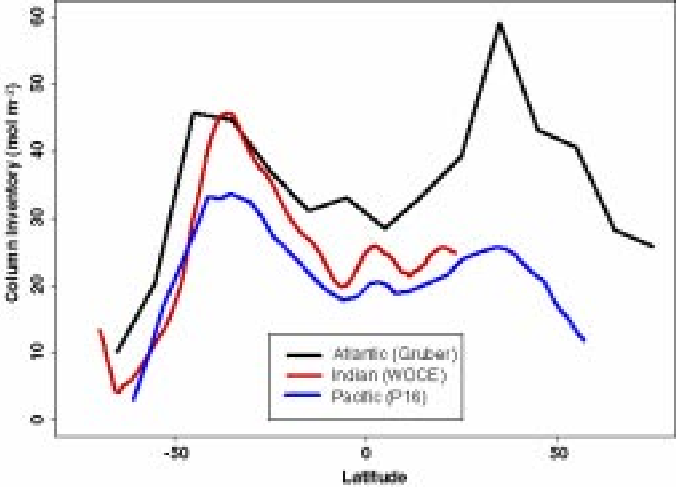
ANTHROPOGENIC CO_2 INVENTORIES

The oceanic anthropogenic CO_2 uptake estimates used by the IPCC in constructing global carbon budgets are based on indirect methods such as ocean circulation models calibrated or validated with tracer observations (e.g., bomb radiocarbon; see Schimel et al. 1996). The uncertainty associated with the average uptake is estimated to be ± 40 percent. Estimates of oceanic anthropogenic CO_2 based on direct measurements of carbon in the oceans have been limited by the paucity of high-quality data and adequate techniques for isolating the anthropogenic component.

In the 1990s, the cooperative multi-agency efforts of the World Ocean Circulation Experiment (WOCE), Joint Global Ocean Flux Study (JGOFS), and Ocean-Atmosphere Carbon Exchange Study (OACES) together with parallel international programs greatly improved the global ocean carbon database. Total carbon dioxide (TCO_2) data sets accurate to 2-3 µmol/kg, equivalent to approximately 2 to 3 years' uptake of anthropogenic CO_2 in near-surface waters, are now available for hydrographic transects representing most of the world's oceans. These data, together with recently improved interpretive techniques, will allow a comprehensive global estimate of anthropogenic CO_2 in the oceans that will serve as a bench mark for future observational programs. The spatial distribution of the data-based inventory estimates also provide robust constraints for the evaluation of prognostic ocean carbon models.

The ΔC^* method of estimating anthropogenic CO_2 was first presented by Gruber et al. (1996) and Gruber (1998) for the Atlantic using GEOSECS, SAVE and TTO carbon data. These results, together with the first basin-wide analysis of the WOCE/JGOFS/OACES carbon data in the Indian Ocean, are shown in Figure 1 as zonal means of the anthropogenic CO_2 column inventories. This figure clearly shows the large North Atlantic sink for CO_2 as well as substantial sinks in the Southern Hemisphere associated with the Subtropical Convergence in both the Atlantic and Indian Oceans. These calculations imply that relatively little anthropogenic CO_2 is stored in the high latitude Southern Ocean. Analysis of the Pacific data is currently underway. A first look at the meridional trends in the Pacific can be

Figure 1. Zonal mean anthropogenic CO_2 column inventories. Atlantic results from Gruber (1998), Indian results from Sabine et al. (1999), Pacific results based on preliminary estimates along P16 (155ºW) only.



estimated from the preliminary column inventory estimates along WOCE line P16 (~155°W). The location of the largest inventories in all three basins are generally consistent with the location of the largest net surface ocean CO_2 sink regions as compiled by Takahashi et al. (1999). The only exceptions are the small peaks in anthropogenic CO_2 at the equator. These regions act as a net sink for anthropogenic CO_2 not because of CO_2 uptake, but because the rising atmospheric CO_2 levels decrease the net outgassing over preindustrial rates. It is interesting to note that despite the predominance of Northern Hemisphere sources for fossil fuel CO_2, the largest accumulation of anthropogenic CO_2 in the oceans interior, when the three ocean basins are combined, is around 30-50°S. Although similar trends can be seen in all three oceans, the details of the distributions are different for each of the basins. How will these distributions change in the future? How might future changes in the atmospheric interhemispheric gradient affect the ocean sink for anthropogenic CO_2?

We can get some feel for how the oceans might change in the future by looking at how they have changed in the past. Estimates of the change in CO_2 inventory between the GEOSECS (1978) and WOCE (1995) surveys in the Indian Ocean suggest that approximately 30% of the total anthropogenic CO_2 inventory has accumulated in the last 18 years (Sabine et al., 1999). This rate of increase is consistent with the percent increase in atmospheric CO_2 over this time period. The distribution patterns for the change in inventory are also very similar to the patterns observed in the total anthropogenic CO_2 distributions (i.e. the largest changes were in the same location as the maximum in total anthropogenic CO_2), indicating that the oceanic increase in anthropogenic CO_2 is keeping pace with the atmospheric increase. Model studies suggest, however, that the oceans will not be able to maintain this pace as the buffering capacity of the ocean decreases with the uptake of anthropogenic CO_2. How will the rate of uptake change in the future? Will all of the oceans respond to higher levels of anthropogenic CO_2 in the same manner? How might feedback mechanisms such as changes in ecosystem structure and/or changes in ocean circulation affect the uptake rate and storage of anthropogenic CO_2 in the future?

RESEARCH NEEDS

Monitoring the evolving anthropogenic CO_2 inventory is an essential long-term component of any effort to understand oceanic CO_2 cycling. Since the oceans have the largest potential to quickly respond to changes in atmospheric CO_2 concentrations, it is important to determine the mechanisms and rates of redistribution of carbon within the water column and to have a program in place to identify any changes as they occur. Global CO_2, tracer and hydrographic surveys are a necessary component of this monitoring network. The sampling time interval for any survey work should provide resolution of the local ventilation time-scales below the main thermocline. The key question, however, is what level of effort is necessary to sufficiently capture future increases in global inventory and possible changes in the rate of uptake? Fully manned scientific cruises have proven to be the most productive and reliable means of data gathering for biogeochemical oceanography, but it is physically demanding and expensive. The future will likely lie in innovative new approaches such as moorings, drifters and profilers, but some level of shipboard work will be necessary in the foreseeable future to validate these approaches. The survey work must be coordinated with the mooring and drifter programs to provide ground-truthing, at least in the development stages, and to reduce ambiguities in interpretation of the temporal variations. Plans for future survey work should also be integrated with other high-frequency sampling networks (e.g.VOS ships) to quantify seasonal and other high-frequency variability that would not be properly constrained by repeat sections. A well thought out cruise plan can provide the backbone that helps to tie together many aspects of the Carbon Cycle Science Plan (CCSP).

Because of the costs of conducting comprehensive surveys like the recent global survey, one proposal that has been put forward is that survey cruises be conducted at a reduced level, but as a continuous effort to reoccupy key lines on a rotating 5-15 year schedule. This is a departure from the "snapshot" paradigm of previous expeditions, but more in line with the directions that related programs are taking. The ongoing survey could exploit strong linkages with other efforts such as CLIVAR (Climate Variability and Predictability program) within GOOS (Global Ocean Observing System) and GCOS (Global Climate Observing System) to make efficient use of ship time. This approach would reduce the annual cost of the monitoring program and would assure maintenance and advancement of the required measurement expertise over the long term.

Figure 2. Map of surface anthropogenic CO_2 concentrations estimated from the NCAR Ocean Model in 1995 (A) and 2005 (B). Points in (A) indicate the location of WOCE/JGOFS/OACES global survey stations. Lines in (B) indicate CLIVAR proposed cruise tracks for future sampling.

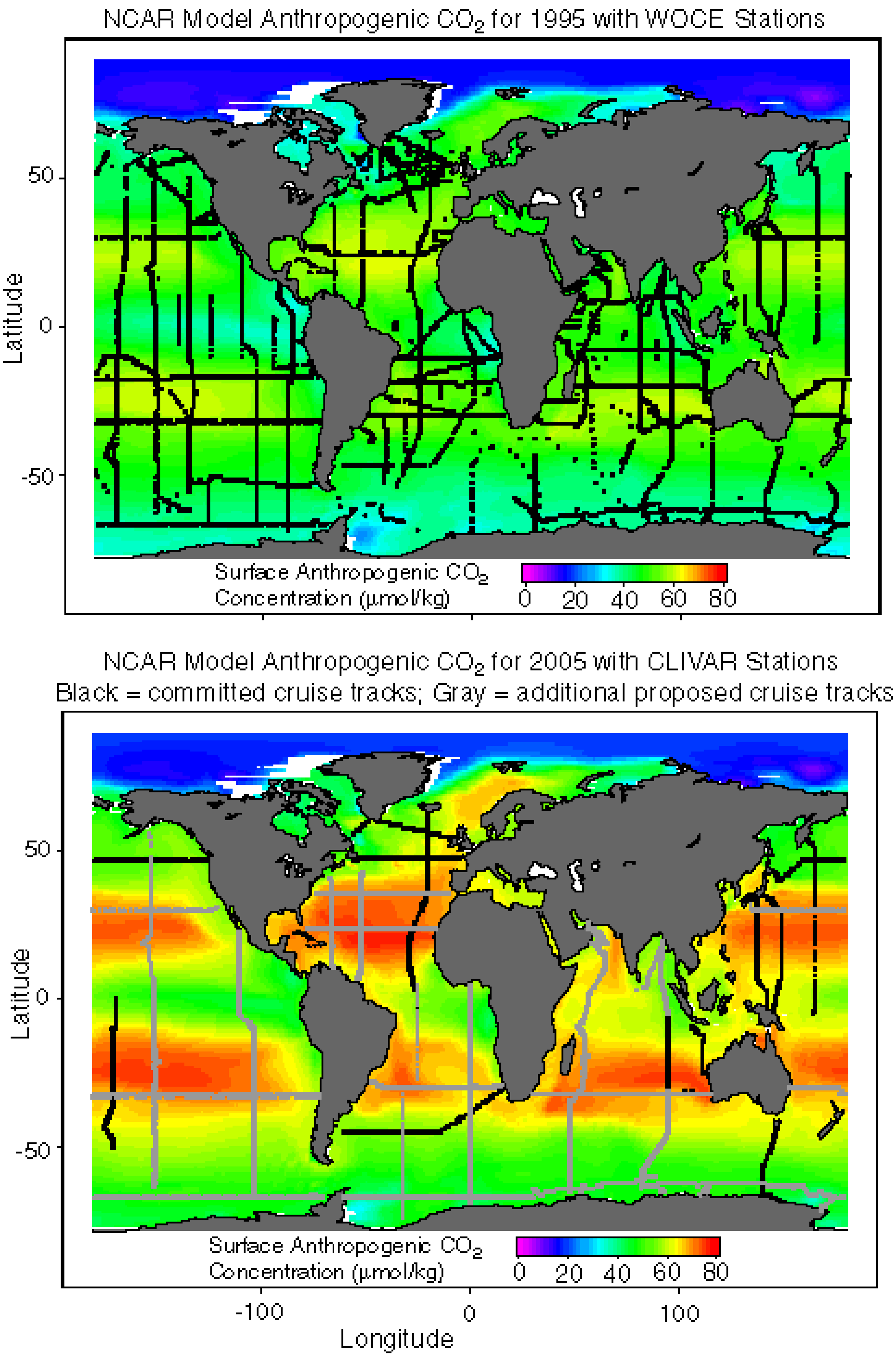


Figure 2 shows a map of surface water anthropogenic CO_2 estimated by the NCAR Ocean Model for 1995 and 2005. The WOCE/JGOFS/OACES global survey stations are shown in figure 2A. CLIVAR has proposed a set of the hydrographic sections (figure 2B), many of them repeats of WOCE Hydrographic Program sections, to be occupied at time intervals of between 5 and 10 years to provide broad-scale global coverage of ocean variability. The proposed CLIVAR survey lines have fewer cruises than the original WOCE survey, but appear to generally cover the primary regions of interest in terms of anthropogenic CO_2. The black lines in figure 2B are cruise tracks that other countries have already committed to monitoring. Some of these projects have planned or are funded to include carbon measurements as part of the core program. The remaining gray lines do not have current commitments. Unfortunately, repeat sections are not currently ranked very high in the US CLIVAR priorities. The physical oceanographic community is looking to the transient tracer community (i.e. anthropogenic CO_2, CFC etc.) to help justify a repeat section program. If the carbon community would like to ensure that a monitoring program is implemented we need to take an active role in promoting the lines we feel are critical to this program and coordinating our efforts with CLIVAR and other activities of GOOS that monitor temporal trends in ocean properties.

In addition to the questions of which lines the US should focus on, we should also think about which measurements are important. The measurement suite must include at least two carbon parameters (e.g. TCO_2 and total alkalinity) and should frequently include a third/fourth CO_2-system property such as pH and/or pCO_2 to assure internal consistency. The continued development and use of Certified Reference Materials (CRM) is essential to this program. Other carbon measurements that should be considered include $\delta^{13}C$ and total organic carbon (TOC) to help provide a mechanistic understanding of the controls on the observed carbon distribution. The standard suite of WOCE quality hydrographic and nutrient measurements is also vitally important along with other transient tracers (i.e., $^3H/^3He$, ^{14}C, CFCs, and HFCs) that can provide information on mixing and transport on various time-scales. Station spacing on the proposed sections should be eddy-resolving to avoid aliasing of eddies and other variability into the climate signal. Meridional sections are important for understanding variations in basin-scale circulation patterns and inventory changes. Sections need to be run from coast to coast to facilitate transport calculations. Repeat occupation of zonal sections allows for the detection of variability in the rates, pathways, and properties of deep and intermediate waters carried towards the equator from the high latitudes. Ideally, they should be located downstream of the deep and intermediate water formation regions.

Ultimately, the plan that is implemented will involve a compromise between the sections necessary to properly monitor the evolving anthropogenic CO_2 inventory and the level of funding that will be available to support this work. The timing is also somewhat dependent on what questions one is trying to address. A 5-year repeat cycle is ideal for transport estimates. Longer intervals will increase the signal to noise ratio for detecting the anthropogenic increase. The OCTET working group needs to identify and prioritize which lines the US will commit to and integrate that plan with the overall goals of the CCSP.

Research Themes for OCTET

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The natural radiocarbon research group at the Lawrence Livermore National Laboratory Center for Accelerator Mass Spectrometry performs approximately 9500 high precision (3-5‰) AMS ^{14}C measurements each year. A significant fraction of these measurements are on oceanographic samples for a variety of in-house and collaborative projects, in addition to fee for service work for outside oceanographers and geochemists. We have identified some key research themes which we believe are relevant to the goals of OCTET, where present knowledge is lacking and ^{14}C measurements will play a significant role.

^{14}C as a tracer for atmosphere-deep ocean carbon transport

Atmosphere-ocean CO_2 transfer and the transport of carbon to deeper waters via the solubility and biological pumps are the two dominant steps in determining ocean uptake of atmospheric CO_2. Because ^{14}C produced in the atmosphere is transferred to surface waters as $^{14}CO_2$ and subsequently transported to depth, ^{14}C provides a unique tracer of carbon and water movement within the oceans. Indeed, because the residence time of water in the deep ocean allows for significant radioactive decay, the ^{14}C distribution in the surface ocean is particularly sensitive to vertical exchange processes. In addition, nuclear weapons testing in the '50s and early '60s produced an atmospheric bomb-^{14}C pulse that has provided an an invaluable additional transient tracer.

While past and future open-ocean direct sampling programs (eg.GEOSECS and WOCE) provide snapshots of the state of the ocean, such measurement programs may lack spatial coverage, and have all occurred after peak bomb ^{14}C levels were reached in surface waters at most locations. Moreover, snapshots of “dye-type” transient tracers miss the dynamic nature of the system. Model comparisons that appear to match such snap-shots, and return a "consensus" ocean uptake of anthropogenic carbon, may have done so by inaccurate means and should not be exclusively relied upon.

A further reality check for models and an important corollary to major sampling and measurement campaigns is to develop oceanographic $\Delta^{14}C$ time series to help reconstruct spatial and temporal variations in CO_2 exchange as well as utilize the $\Delta^{14}C$ as a tracer reflecting intra-annual to cenntenial-scale ocean circulation changes. In particular, the timing, amplitude and shape of the post-bomb $\Delta^{14}C$ maximum provides far stronger constraints on CO_2 exchange and the transport of carbon out of the mixed layer than can be obtained from snapshot data. Such records are conventionally obtained from warm-water archives such as corals, and exisitng efforts in this direction should be continued and expanded. In addition, however, banded mollusks and other calcareous organisms, fish otoliths, and dried (and perhaps even preserved) organic materials are all worthy of investigation as potential recorders of conditions in colder waters, including those of the sub-polar oceans and the thermocline.

Such archives can also be used to develop pre-bomb surface water ^{14}C distributions to document the regional variations in the natural processes which combine to determine regional surface water ^{14}C levels: 1) atmospheric $^{14}CO_2$ exchange, 2) the removal to depth of "isotopically equilibrated" carbon from the surface waters, and 3) the upwelling of ^{14}C- depleted waters into the mixed layer - an important process for priming the biological pump. The pre-bomb data also provide the baseline required for detailed study of the ingress of the bomb radiocarbon transient. When combined with the direct sampling "snapshot" campaigns these data sets and time-series will provide very powerful constraints on the processes which move carbon from the atmosphere into the surface ocean and transport it to depth.

DOC and the role of rivers in the ocean carbon cycle

Storage of organic carbon in the ocean is a major sink in the carbon cycle, involving both long-term storage of C in ocean sediments and shorter term storage in particulate (POC) and dissolved organic carbon (DOC). Understanding these storage processes is crucial to understanding the effects of human C cycle perturbations, and ^{14}C provides key information on the timescales of storage processes. Ocean sediments are the final OC repository and the chemistry of OC stored in sediments is poorly constrained. In the water column, DOC is the largest exchangeable organic carbon pool in the ocean, dwarfing particulate organic carbon (POC) by over an order of magnitude. Sources and sinks of DOC are only beginning to be constrained, and understanding the timescales of these sources and sinks is essential in the development of even the most basic C cycle model.

Both sediments and DOC may receive more of their OC from terrestrial sources than has been previously recognized. Terrestrial OC derived from biomass burning (black carbon) has been indentified as up to 30% of ocean sedimentary organic carbon in some sites, but mechanisms to transport this material to the deep ocean remain poorly understood, and measurement techniques have yet to be standardized. Methods to measure mass and ^{14}C in fractions of organic carbon in the ocean (sedimentary as well as “pelagic”) need further development and standardization. Following this, these techniques should be applied to answering questions of:

1) sources of OC stored in DOC and sediments;

2) fate of OC entering DOC and sediments, (inc.remineralization processes)
3) identification of OC transport mechanisms (e.g. aerosol, river, benthic storm transport)
4) timescales of storage and transport processes

In particular, rivers deserve a second look as a source of OC to the ocean. Although rivers export enough DOC to account for the entire ocean DOC pool, bulk measurements of organic carbon and organic carbon ^{13}C and ^{14}C from large rivers do not support the hypothesis that rivers are a source of DOC. However, several lines of evidence suggest that the issue of rivers in the ocean's carbon cycle needs revisiting.

1) Smaller, high-relief rivers deliver sediment much more effectively to the ocean and are geochemically almost entirely unstudied;
2) compound-specific ^{13}C studies show that some OC is transported long distances off shore and that bulk ^{13}C measurements are not good terrestrial OC indicators;
3) Initial ^{14}C and geochemical studies of small, high-relief rivers show export of old, refractory soil carbon.

Non-coral calcareous organisms - an overlooked component of the carbon cycle?

A fundamental question of ocean carbon cycle research is closure of the oceanic carbon cycle over timescales relevant to anthropogenic perturbations, as well as over geologic timescales. Of particular importance is the role of carbonate secrecting organisms, which in the process of forming calcium carbonate use up alkalinity with the "release" of aqueous CO_2 as a byproduct. Quantification of the inorganic carbon budget has traditionally included particulate carbonate formation and export from the surface to deep ocean with compensation at depth to account for dissolution of sedimentary calcium carbonate (foraminifera, coccolithophorids, pteropods). Coral reefs (traditionally hermatypic reef-builders) with associated carbonate hardgrounds "shed" excess carbonate to deeper depths, usually without the associated compensation due to the export depths being above the calcite and aragonite lysocline.

A previously under-appreciated component of the ocean's DIC cycle is that of calcareous algae (eg. rhodoliths) and other non-coral calcareous organisms. Unlike the traditionally accounted-for tropical carbonate systems, the calcareous algae have a global distribution. Although living densities are not well constrained, recent studies utilizing $\Delta^{14}C$ derived rhodolith growth rates have placed a conservative estimate of the carbonate production at 0.5 GtC/yr; the same order of magnitude as pelagic carbonate and coral reef production. The possible influence of coral reef growth on the carbon cycle has received attention, but the effects of other calcareous organisms have been largely neglected. Better quantification of the carbonate accretion (aka growth) rate and more detailed mapping of the spatial distribution and percent living cover is necessary to adequately constrain this portion of the carbon budget.

Paleoclimate paleo-carbon cycle interactions: ^{14}C as a tracer & chronometer

Our current knowledge of the ocean carbon cycle response to climate variability and the feedbacks to climate is disturbingly incomplete. For example, the following questions remain open:

1) What was the state of the glacial ocean and how does this relate to atmospheric CO_2 drawdown?
2) Are the factor of 2 changes in ^{14}C in marine and terrestrial records from Isotope Stage 3 a signature of Heinrich event disturbances affecting the carbon cycle?
3) What happened to the carbon cycle during the Pleistocene-Holocene transition?
4) Are Holocene centennial-scale ^{14}C variations fully explained by production rate changes, or did associated climate and ocean circulation changes affect the carbon cycle?

Until we can effectively answer these and similar questions, there will be doubts about how much natural climate (and carbon cycle) variability underlies any response to anthropogenic forcing, and about our ability to predict future changes. It is increasingly necessary to not only be able to reconstruct past climate and carbon cycle changes in broad brush strokes but to be able to look at regional scale variability with a frequency pertinent to a human life span. Also, and very importantly, the paleoclimate/paleo carbon cycle observations and data syntheses required for those answers will provide data to test models under conditions which are realistic but markedly different from those of today.

Marine archives such as sediments and corals contain both paleoclimate records and ^{14}C carbon cycle proxies. Surface and in some cases bottom water DIC ^{14}C can be recovered from carbonates (corals, forams, etc), and marine DOC and terrestrial ^{14}C records may also be recoverable from sediments using compound-specific techniques. Radiocarbon measurements on these different materials (eg, marine-terrestrial or surface-deep ocean) can provide tracer information for the paleo-carbon cycle, and this can be unequivocally linked to paleoclimate information from the same sediments to test hypotheses concerning climate and carbon cycle links.

Where independent chronologies exist, as in varved anoxic sediments or U-Th dated corals, ^{14}C records for the different reservoirs can be extracted and used to explicitly study the carbon cycle and its relationship to variable climate. Moreover, such independently dated records can also provide the improved ^{14}C calibration data required for linking the body of radiocarbon-dated paleoceanographic records into a detailed common temporal framework with calendric archives such as ice cores. Such improvements are necessary to understand in detail the sequence of changes involved in the Pleistocene-Holocene transition. An expanded effort is required to identify suitable marine archives which can provide data to address these issues, to extract relevant paleoclimate and ^{14}C records, and to develop the best possible ^{14}C calibration datasets.

Active biotransport of organic and inorganic carbon by zooplankton diel vertical migration

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Zooplankton play a well-documented role in the biological pump by feeding in surface waters and producing sinking fecal pellets. Diel vertically migrating zooplankton and nekton also play an important (and less understood) role in vertical flux by consuming organic particles in surface waters at night and releasing a portion of the ingested carbon below the mixed layer upon their decent to depth at dawn. This active transport occurs in several ways:

1) Respiration of inorganic carbon at depth (e.g., Longhurst et al., 1990; Dam et al., 1995; LeBorgne and Rodier,1997)
2) Excretion of dissolved organic carbon at depth (Steinberg et al. 2000)
3) Defecation at depth (e.g., Morales et al. 1993; Atkinson et al.1996)
4) Molting at depth
5) Loss due to mortality (predation or senescence) at depth (e.g., Longhurst and Williams, 1992; Zhang and Dam 1997)

Table 1 shows the studies to date that demonstrate vertically migrating zooplankton can actively transport a significant amount of dissolved inorganic carbon (and nitrogen) to deep water, which can be significant relative to the gravitational vertical export of sinking particulate organic carbon measured with sediment traps. What we don't know as well is # 2-5 above. When potential for organic excretion, defecation, mortality, and molting at depth is considered, estimates of active transport has the potential to more than double current estimates.

This process is important within the OCTET framework as changes in vertical flux across the pycnocline must reflect changes in rates of biological processes in the euphotic zone, and thus ultimately effects the rate at which CO_2 is drawn down into the surface ocean. Like the sinking flux of organic C, active flux will partially contribute to the draw down of atmospheric CO_2. This flux across the pycnocline is to a reservoir with a residence of ~ 1000 years. How might this change in a warmer, more stratified ocean? It is hypothesized that reductions in passive export production will occur. "Interzonal migrants" may not be affected by increased surface stratification (especially if they are not dependant on sinking flux as non-migrators living at depth are), and could become relatively more important in sequestration of carbon in the deep ocean.

How do we narrow the uncertainties in this measurement?

Where geographically is flux by vertical migrants most significant?

Relative to particle flux, the prediction is that migrant active fluxes are more important in oligotrophic regions where a large fraction of the resident zooplankton community migrates and passive particle flux is relatively low. However, absolute migrant fluxes in a particular region should be more significant in meso- and eutrophic areas with significantly higher overall migrating zooplankton biomass. There are few measurements of migratory flux in meso- and eutrophic regimes.

Over what spatial and temporal scales must measurements be made?

Measurements should be made on both diel and seasonal time scales. Data from both the JGOFS time-series stations show night:day ratios of zooplankton biomass in the euphotic zone varies significantly (e.g., at BATS N:D ratio ranges from <1 to 3.4). Migrating biomass also varies significantly between seasons (i.e. spring is normally highest). In addition, the contribution of seasonal (as opposed to diel) vertical migrations to carbon flux has only been calculated for the North Atlantic, and it has recently been demonstrated that active transport by seasonal migrants is more important there than originally estimated (Morales et al. 1999).

How would you scale measurements of active flux by vertical migrants to regional or global scales?

On a regional scale, the biomass of the migrating community (night minus day biomass in the euphotic zone) is measured (and should include different seasons). Weight-specific respiration or excretion rates are then determined to apply to the migrating biomass. These are either experimentally determined for the appropriate temperature migrators experience at depth in the region, or available algorithms for weight & temperature-dependent zooplankton metabolic rates (e.g., Ikeda 1985) are applied to the migrating biomass. Another approach is to measure diel changes in organic C (or N) content of migrators. This is done by comparing body C or N content in individual migrators caught in the surface waters at dusk (when body C or N is at a minimum prior to onset of feeding) with those caught at dawn (when weight is maximum just after feeding and prior to dawn decent) (Hays et al. 1997).

Longhurst (1990) provides examples of two ways of extrapolating active flux by vertical migrants on a global, ocean basin scale. The first is to apply ratios of active migrator flux: passive sinking flux in areas with known sinking flux. A problem with this approach is the significant range in these ratios amongst the studies published so far (Table 1). Much of this variation results from the seasonal changes in zooplankton biomass and particle flux, and the time of year individual studies were conducted. A second approach is to use biomass estimates of the migrating zooplankton community and apply published temperature-dependent zooplankton metabolic rates for broad temperature regions in different basins. The challenge of this approach is while there may be decent (maybe) global epipelagic zooplankton biomass data, only for some regions do we have good estimates of the migrating biomass. In addition, as mentioned above, while there is good information on zooplankton inorganic respiration and excretion rates, there are still few measurements on organic excretion rates, mortality rates at depth, or active POC transport by defecation at depth.

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Table 1. Studies to date measuring the ratio of downward transport of carbon by diel migrating zooplankton to gravitational POC fluxes measured by sediment traps. Migratory and sediment trap fluxes are calculated across 150 m or the depth of the euphotic zone. Mean, and range (given in parentheses). (Data not listed here were not provided, or unclear, in reference).

Location of study and time of year	Migrating biomass (mgC m^{-2})	Migratory flux (mgC m^{-2} day^{-1})	% of mean POC flux	Reference
Subtropical & tropical Atlantic- several stations (September)	_	5.5 (2.8-8.8)[a]	6 (4-14)	Longhurst *et al*. (1990)
BATS (March/April)	191 (82-536)	14.5 (6.2-40.6)	34 (18-70)	Dam *et al*. (1995)
Equatorial Pacific: (March/April)	96	4.2[b]	18	Zhang and Dam (1997)

(October)	155	7.3[b]	25	
Equatorial Pacific:				LeBorgne and Rodier (1997); Rodier and Le Borgne (1997)
oligotrophic	47[c]	3.8[a,e]	8[d]	
HNLC area	53[c]	7.9[a,e]	4[d]	
(September/October)				
North Atlantic (NABE)	(5-480)	–	(19-40)	Morales (1999)
BATS (year-round)	50 (0-123)	2.0 (0 -9.9)[e]	8 (0-39)	(Steinberg *et al.* 2000)
HOT (year-round)	142	3.6 (1.0 -9.2)	15 (6-25)	Al-Mutairi and Landry (in press)

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[a] Includes migrating micronekton or nekton in addition to zooplankton.

[b] Does not include flux due to mortality (although it is estimated in study)

[c] Calculated from Table 10, LeBorgne and Rodier (1997), assuming C= 0.4* dry weight

[d] Calculated from Table 8, Rodier and Le Borgne (1997)

[e] Migratory flux includes DOC + CO_2 (values in other studies are respiratory flux only).

BIOLOGICAL AND TEMPERATURE EFFECTS ON SEA SURFACE pCO_2 OVER THE GLOBAL OCEANS

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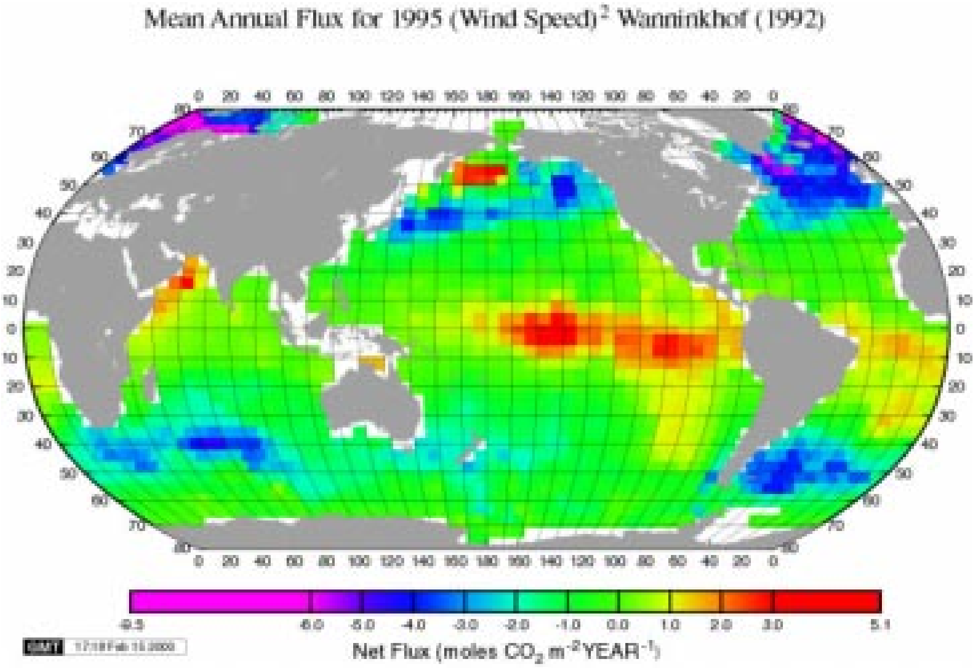
OBJECTIVE:

In order to provide background information for facilitating our discussion at the upcoming OCTET meeting, I have prepared several global distribution maps for surface water pCO_2 based upon about 500,000 sea surface pCO_2 measurements currently present in my data bank. The effects on surface water pCO_2 of seasonal changes in SST and biological CO_2 utilization are presented. The numerical method developed for constructing these climatological distribution maps for surface water pCO_2 over the global ocean has been described in Takahashi et al., 1995, Takahashi et al., 1997 and Takahashi et al., 1999).

GLOBAL SEA-AIR CO_2 FLUX:

The mean annual sea-air CO_2 flux (4° x 5° resolution) for the reference year 1995 is shown in Fig. 1. This was constructed using data excluding the El Nino year data obtained over the equatorial Pacific between 10°S and 10°N and hence represents a climatological mean distribution of the net sea-air flux for non-El Nino years. For the computation of the net sea-air CO_2 flux, the mean monthly sea-air pCO_2 difference data, the CO_2 gas transfer coefficient vs. wind speed relation formulated by Wanninkhof (1992) and the mean monthly wind speed of Esbensen and Kushnir (1981) were used. The ocean sink areas for atmospheric CO_2 are shown in blue and the source areas are in red. The sink areas are due mainly to the cooling of poleward flowing warm waters and the biological utilization of CO_2; whereas the source areas are due to upwelling of CO_2-rich deep waters and warming of the upwelled waters. The global ocean uptake for CO_2 thus estimated is 2.0 Gt-C/yr.

FIG. 1



CONTRIBUTIONS OF SEASONAL SST AND BIOLOGY CHANGES:

The magnitude of surface water pCO_2 depends primarily on SST, the biological drawdown of CO_2 and the upwelling of deep waters rich in CO_2 and nutrients. From the equator to the pole, SST changes by 32 °C. Since the pCO_2 in a parcel of seawater doubles every 16 °C, sea surface temperature changes should change pCO_2 by a factor of 4. Over the global ocean, the TCO_2 concentration changes by about 250 umol/kg due primarily to biological utilization of CO_2 and upwelling. This should change the pCO_2 by a factor of about 3. Since the seasonal effects of SST changes are out of phase and are of similar magnitude as the biology effects, they tend to cancel each other partially or entirely depending on the oceanographic setting.

Using the seasonal pCO_2 and SST data, I have separated seasonal contributions on pCO_2 due to SST changes and those due to net biological utilization of CO_2 using the following methods. For each 4° x 5° pixel, we have the mean annual pCO_2 value and monthly SST values. Using a temperature effect on seawater pCO_2 of 4.23 % per degree C (Takahashi et al., 1993), we computed the seawater pCO_2 values for February and August for the northern hemisphere pixels. The difference between these two values (August – February for the northern hemisphere pixels and February – August for the southern hemisphere pixels) represents the magnitude of seawater pCO_2 attributable to seasonal SST changes alone. The global distribution of the SST effect on seawater pCO_2 thus computed is shown in Fig. 2. It shows that the seasonal SST effects are large in the temperate zones in the North Pacific and North Atlantic, reaching up to 170 uatm. The effects are especially large over the confluence areas of the cold Oyashio with the warm Kuroshio in the North Pacific and the cold Labrador Current with the warm Gulf Stream in the North Atlantic reaching 230 uatm. Those for the southern temperate oceans are not as large as the northern counterparts. The seasonal SST effects are small over the tropical and subpolar/polar oceans.

FIG. 2

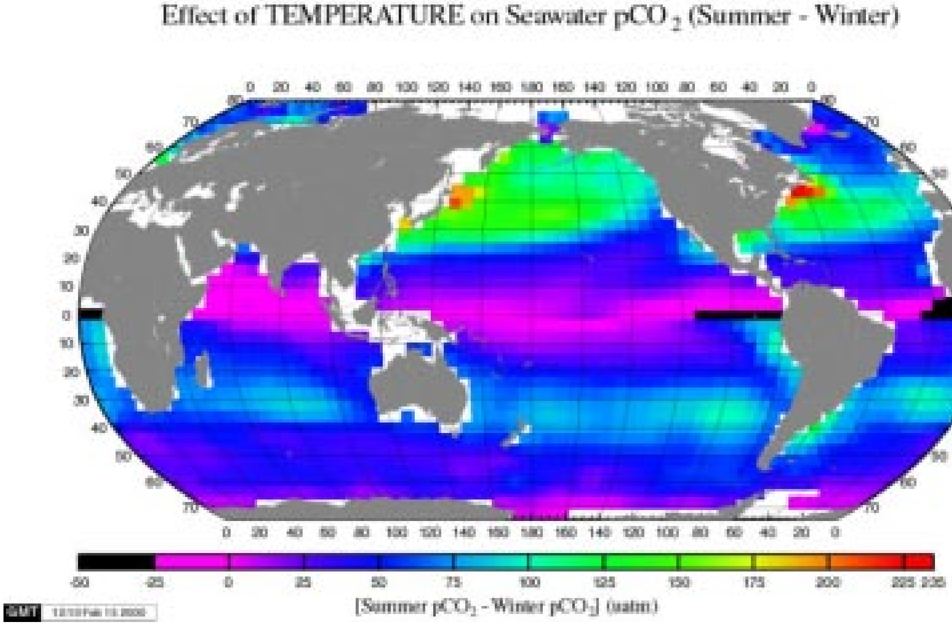
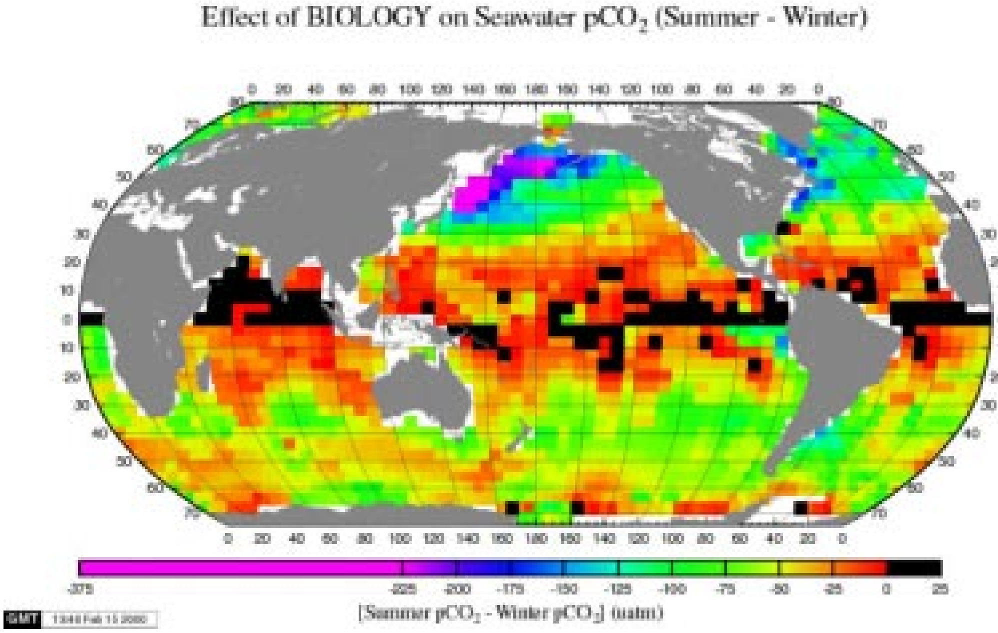

Effect of TEMPERATURE on Seawater pCO_2 (Summer - Winter)

Fig. 3 shows the distribution of the seasonal pCO_2 changes attributable to the apparent biological utilization of CO_2. It should be pointed out that the effects of seasonal changes in the CO_2 flux supplied to the euphotic zone by the upwelling of deep water are implicitly included. Hence, the quantity in this figure is an “apparent” biological utilization effect on surface water pCO_2 representing a minimum estimate for the biological utilization. The map was computed as follows. Using the mean pCO_2 value for each month, the mean monthly SST and the mean annual SST for each 4° x 5°

pixel, the pCO_2 value at the mean annual SST was computed using the SST data and the temperature effect on seawater pCO_2 of 4.23 % per degree C (Takahashi et al., 1993). The effect of seasonal changes in SST on surface water pCO_2 is removed. Therefore, the

FIG. 3

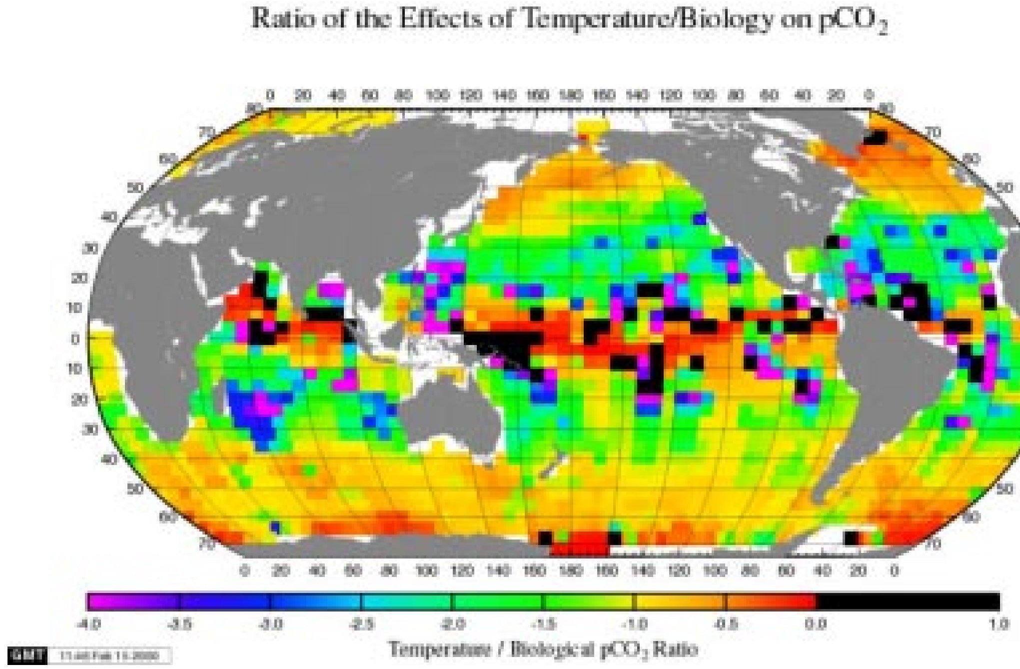


summer-to-winter difference in the pCO_2 values normalized to a constant temperature represents the effect of biology on pCO_2 in seawater. The difference between the August and February values is plotted in Fig. 3. It shows that he biological effects are small over tropical areas, whereas they are large over temperate and high latitude areas. The black pixels in tropics indicate the areas where seasonal changes are not simple sinusoidal but complex due to various oceanographic processes such as seasonal monsoons (Arabian Sea) and equatorial upwelling. Three black pixels located around Antarctica represent the lack of seasonal data.

Fig. 3 shows that broad temperate gyre areas both in the northern and southern hemisphere oceans exhibit large biology effects on surface water pCO_2 of about –100 uatm. The minus sign indicates that the biology effect is opposite to the SST effects.
The confluence areas of the cold and warm waters located in the western North Pacific and Atlantic show very large biological effects (exceeding –225 uatm). These areas coincide with the large SST effects (see Fig. 2). The warming effect on pCO_2 during the summer counteracts the strong lowering effect by summer photosynthesis occurring within the thermally stratified surface layers.

Fig. 4 shows the ratio of the SST effect and biological effect on pCO_2. Ratios between 0.0 and –1.0 indicate the areas where the biological effects exceed the SST effects, and those between –1.0 and -4.0 indicate the areas where the thermal effects exceed the biological effects. The equatorial Pacific and the high latitude Southern Ocean are areas where seasonal pCO_2 changes are predominantly driven by biology. Most importantly, the boundaries between the yellow and green areas (where the ratio is –1.0) separate the thermally controlled zone from the biologically controlled zone.

FIG. 4



SUMMARY

On the basis of surface water pCO_2 observations, monthly distribution maps showing the climatological distribution of surface water pCO_2 over the global ocean have been constructed for a reference year 1995. The seasonal changes of pCO_2 have been attributed to the effect of seasonal SST changes and that of seasonal biological utilization of CO_2. The effects of seasonal changes in deep water upwelling are implicitly included in the biological contributions. Based upon the distribution maps presented, the following oceanic areas where the seasonal pCO_2 changes are dominated by biological effects can be identified;

Northwestern North Pacific,
Northwestern North Atlantic,
Equatorial Pacific (JGOFS/Eq.Pac),
Arabian Sea (JGOFS/Arabian Sea),
Ross Sea (JGOFS/AESOP)
Weddell Sea and southern South Atlantic, and
Southern South Indian Ocean.

Of these areas, three of them have been investigated intensely by the projects indicated within the parentheses. Although the eastern North Atlantic has been studied during the JGOFS/NABE project, the western subarctic Atlantic has not been investigated. Furthermore, mechanisms with which nutrients and CO_2 are supplied to the euphotic zone over the subtropical gyres (such as the

Sargasso Sea) have not been understood clearly in spite of the intense research efforts being made at the BATS and HOT sites.

The information presented in this report may serve for selecting preferred study areas for the OCTET project.

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On Fluxes and Interfaces

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A central objective of the Carbon Cycle Science Plan is to quantify fluxes between the atmospheric, terrestrial and oceanic carbon reservoirs. In most basic terms the flux is defined as the mass of a compound crossing an interface per unit time Thus, to quantify the ocean fluxes we must:

- Define the interface
- Assess which components of the oceanic carbon system contribute significantly to the flux
- Determine what processes control the flux at the interface of choice

The choice of interface depends very much on the timescale on which we wish to study the exchange processes of interest. In addition, in case of investigation of transformations by mass balance approaches transports over several interfaces have to be quantified.

Relative to connections of the open ocean to the atmospheric carbon reservoirs there are three primary interfaces of interest for transport on seasonal to decadal time scales:

- The air-sea interface
- The bottom of the seasonal mixed layer
- The bottom of the winter mixed layer

For longer timescales the fluxes across water-sediment interface are important as well.

The total flux of carbon across each of the interfaces are driven by different factors and involve different biotic and a--biotic carbon species. For implementation of ocean carbon based programs like OCTET it is thus imperative that all components of the flux process are accounted for at the interface of choice.

Fluxes across the air-sea interface offer the opportunity to study processes on daily to monthly timescales and local space scales. There is the possibility to extrapolate to longer time and larger space scale with the appropriate approximations and algorithms relating the relevant flux parameters to other parameters. Parameters necessary to determine these fluxes are the pCO_2 difference between upper ocean and lower atmosphere (ΔpCO_2) and the gas transfer velocity. Although the relative ease of observation and extrapolation by, for instance, remote sensing products makes it an interface of choice, the large variability on short terms can serious bias results.

Fluxes across the base of the seasonal mixed layer offer a more integrated picture of carbon fluxes on seasonal timescales but require knowledge of several fundamentally different exchange processes such as settling, diffusion, entrainment and possibly active migration of "living" carbon stocks across the interface. A comprehensive flux measurement scheme will involve measurements of sinking particles [with sediment traps], and measurement of advection and diffusion in conjunction with dissolved inorganic and dissolved inorganic carbon gradients across the interface.

The winter mixed layer boundary is of prime interest for study of carbon fluxes on annual to decadal timescales. The challenges are much the same as for study across the seasonal mixed layer except that this interface is generally less energetic and often beyond the vertical migration zone of critters. Chemical gradients and diffusive processes are often more constant over time.

Measuring a component of the flux, for instance, particle settling in isolation of diffusive fluxes, can lead to serious misrepresentation of total fluxes. The situation is often confounded by the coupling of fluxes, sometimes with a time delay. With a renewed interest in programs to study the different aspects global carbon cycling and perturbations therein a comprehensive approach to flux determination is advocated.

Long-term, basin and global observing strategies

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What CLIVAR and GOOS plan for long-term, basin and global observing strategies

In order to provide a basis for discussion of how long-term, large scale observational strategies for OCTET might be integrated with those of CLIVAR and the climate component of GOOS, a summary of the plans being developed for those programs is provided. Both CLIVAR and the climate component of GOOS have to date concentrated on the observation of the physical (temperature, salinity, velocity; heat, freshwater, and mass transports and storage) components of the climate system. However, both have had discussions about how to better integrate carbon observations; and it is timely for a dialog to be established.

Both CLIVAR and GOOS (hereafter, meaning the climate component of GOOS) are planning large scale, long-running observational efforts. Spatial coverage would have as its observational base data obtained through the use of remote sensing, surface drifters, drifting floats that would rise to the surface every 10 to 14 days and otherwise park at 1500 to 2000 m depth (ARGO floats), and volunteer observing ships (VOS) and the fields of surface meteorology produced by numerical weather prediction (NWP) models. High temporal and vertical resolution in the ocean would be obtained from a select number of moorings, which would also be used to sample boundary current and equatorial regions that could not be well-sampled by Lagrangian methods.

Plans for the global sampling call for 3000 ARGO floats, distributed roughly every 3 degrees latitude/longitude. These floats would have ~5 year life and presently carry temperature and salinity sensors. Together with satellite altimetry and scatterometry, they would provide the basis for global maps of the physical state (temperature and salinity) of the ocean and of the ocean’s geostrophic and wind-driven currents. One strategy for keeping a watch on the calibration of the floats calls for using the more stable T/S variability found at the parking depth. T/S variability at that depth and at greater depths will be monitored at isolated points by long-term moorings that can observe the full water column. These moorings, which would number roughly 10 per ocean basin exclusive of the TAO and PIRATA arrays, would also provide the means to examine eddy transports and processes with short space and time scales not resolved by the Eulerian array and remote sensing. In the upper 1500 to 2000 m, it is planned that the physical data would be assimilated using models so that maps of these fields could be produced for distribution to other users. There has not yet been a strong consensus that the global hydrographic survey carried out in WOCE should be routinely repeated. The suggestion has been that the case for such sampling needs to be made in concert with tracer studies, assessments of carbon inventories, and model development and verification efforts.

CLIVAR and GOOS also plan to measure the surface exchanges of heat, freshwater, and momentum. Broad scale coverage will come from in-situ and remote sampling as well as from the gridded fields from the NWP models. Remote sensing is looked to particularly for use in developing the surface wind, SST, shortwave and longwave radiation, and precipitation fields. NWP model fields will provide the surface humidity, pressure, and air temperature fields as well as another source for surface wind fields. Bulk formulae will be used to determine the components of the net heat flux (latent, sensible, shortwave, and longwave) and the wind stress. Satellite fields of precipitation would be used in conjunction with the latent heat flux fields to produce estimates of the freshwater flux. It is known that these global fields have errors that can be large. ECMWF and NCEP monthly mean net heat fluxes in the Arabian Sea were biased low by 50 to 100 Watts per square meter, for example. Thus, it will be essential to deploy additional in-situ observing platforms to provide the means to calibrate and adjust the model and satellite fields. These calibration platforms will be of two types: surface flux reference sites at fixed locations and well-equipped VOS making regular, cross-basin transects. The surface flux reference sites will be long-term surface moorings instrumented to make high quality surface meteorological measurements (wind speed and direction, air and sea surface temperature, incoming shortwave, incoming longwave, precipitation, barometric pressure, and humidity). These few sites (~5 to 10 per ocean basin) would identify errors in the model and satellite fields to support adjusting those fields as well as improvements to the NWP models and to the remote sensing methods. The fixed sites would be complemented by VOS with similar instrumentation that would allow the spatial structure of the errors and uncertainties in the surface meteorological and air-sea flux fields to be examined. Mapping of the air-sea flux fields would be done by using the surface flux reference sites and VOS data to develop correction procedures for the model and satellites data and to provide the information about the space/time scales in the flux fields needed in the assimilation. This procedure may have difficulty in some regimes. Of particular concern are low and high wind regimes, where there is less basis for confidence in the bulk formulae. To resolve these problems, equipping the in-situ surface flux reference sites and VOS with the instruments needed to measure sea state and to make direct measurements of the fluxes is being considered.

Initially, the need is seen for long-term moorings to serve as surface flux reference sites and capture oceanic variability in key locations: where aerosols in the atmosphere compromise estimates of shortwave radiation (such as west of the Sahara), at mid-basin sites characteristic of a large region (such as in the Trades or in the center of the Bermuda-Azores High), at sites of strong air-sea coupling (such as in the Gulf Stream, the Kuroshio extension, and in the Arabian Sea), and at sites where little or now observational basis exists for calibrating models and satellite products (such as in the Southern Ocean), and in sites where horizontal and vertical transports cannot be successfully inferred from a sparse Eulerian array (such as in the equatorial current systems and in western boundary currents).

How would OCTET change these plans?

If these global and large-scale sampling strategies were to be used as well to better describe and understand the storage and transports of carbon within the ocean across the air-sea interface, some additional measurements and further refinements to the strategies are called for. It is hoped that the OCTET workshop would help identify:

1) Additional measurements to be made. What sensors should be considered for the ARGO floats, for the VOS, for drifting surface buoys, for the long-term moorings? Aerosol samplers are being developed for use on surface buoys, as are instruments to measure CO2 flux using eddy covariance methods and pCO2 in the mixed layer. Bio-optical and nutrient samplers as well as sediment traps can now be deployed on Eulerian as well as Lagrangina platforms. What sensors such as these are ready to use and should be considered as standard when planning sampling strategies to support OCTET as well as CLIVAR and GOOS?

2) Siting the long-term reference sites. What role do the long-term moorings play for OCTET? Where should they be sited for maximum benefit? Would they serve primarily as calibration/validation anchor sites or would they support process studies?

3) Deep, repeat sections. What support is there for making repeated deep sections every ~10 years?

4) CLIVAR/GOOS plans for basin scale and global mapping of the physical fields. Do these plans provide the means to map physical elements of the system with time and space resolution sufficient to support OCTET or is higher resolution called for? Will higher space and time resolution be needed to determine the space/time variability of pCO2 in the mixed layer?