OCEAN CARBON & BIOGEOCHEMISTRY SUMMER WORKSHOP Woods Hole Oceanographic Institution, Woods Hole, MA July 23-26, 2007 POSTER ABSTRACTS

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THEME 1. THE INTERPLAY BETWEEN BIOTIC STRUCTURE AND BIOGEOCHEMICAL CYCLES

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M1: Response of bacterioplankton lineages to mixing and restratification in the euphotic and mesopelagic zone at the Bermuda Atlantic time-series study site

At the Bermuda Atlantic Time-series Study (BATS) site regular annual patterns nutrient and DOM distributions, and biological production are influenced by convective overturn. DOC dynamics at BATS demonstrate an annual pattern where DOC stocks accumulate rapidly within the surface 100m are redistributed within the upper 250 m during convective overturn and removed in the upper mesopelagic zone after restratification. Regular annual pattern of prokaryote cell dynamics can also be observed between 140 –250 m at BATS, with cell concentrations increasing during or shortly following convective overturn and persisting at elevated concentrations for several weeks. Here we use Terminal Restriction Fragment Length Polymorphism (T-RFLP), clone library and fluorescent in situ hybridization (FISH) to characterize spatial and temporal patterns in bacterioplankton lineages that respond to these mixing / stratification events. Nonmetric multidimensional scaling of monthly surface and 200 m bacterial 16S rDNA T-RFLP fragments from 1992 to 2002 revealed temporal trends in bacterial community structure within the different depth horizons. T-RFLP fragments matching cloned OCS116, SAR11, and marine Actinobacteria fragments exhibited the strongest 200 m increases following convective overturn suggesting that members of these groups may be important in DOC dynamics in the upper mesopelagic zone. Increases in SAR11, SAR86, and SAR116 fragments exhibited the strongest surface increases during summer periods. Quantitative FISH estimates of the bacterial lineage SAR 11 demonstrate a spring maximum shortly after seasonal stratification and

another maximum that developed in the summer. These data lend support to previous observations seasonal shift in SAR11 subclusters from spring to summer and suggest the annual SAR11 bifurcated maximum may represent a shift in SAR11 composition.

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M2: Phytoplankton community composition, nutricline depth, and mixed layer dynamics in the ocean

Over the past two hundred millions of years diatoms and coccolithophorids have been central players in marine biogeochemical cycles. In modern oceans, diatoms contribute ~40% of global oceanic net primary production and a proportionately high fraction of the organic carbon exported to the ocean interior. Coccolithophorids, through the formation of calcite shells, alter the equilibrium of the inorganic carbon system and alkalinity of seawater, and hence limit the ocean's potential to absorb atmospheric carbon dioxide. Despite the importance of these phytoplankton functional groups to marine biogeochemical cycles, the mechanisms that control their global oceanic distribution remain poorly understood. Here we analyze phytoplankton community composition across latitudinal gradients in the Atlantic Ocean to show that the distribution of diatoms and coccolithophorids is critically dependent upon the nutricline depth and upper mixed layer dynamics. Observations show that, in response to increased ocean stratification, 50-m shoaling of the upper mixed layer results in a 1.5-fold increase in coccolithophorid biomass and number of species relative to diatoms. Because these two phytoplankton functional groups contribute disproportionately to the export of carbon in the ocean, our results allow us to assess the impact of seasonal variations in ocean stratification or climate-driven changes in ocean circulation on the particulate inorganic to organic carbon rain ratio. These findings provide insights into how phytoplankton community composition may respond to changing ocean scenarios with profound implications on Earth's climate.

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M3: Carbon dioxide system and net community production within a cold-core cyclonic eddy in the lee of Hawaii

The cycling of dissolved inorganic carbon (DIC) and processes controlling air-sea CO₂ exchange were investigated within a mature cold-core cyclonic eddy, Cyclone *Opal* that formed in the lee of the main Hawaiian Islands in the subtropical North Pacific Gyre. Within the eddy core, physical and biogeochemical properties suggested that nutrient-rich deep waters were uplifted by ~80 m relative to surrounding waters, enhancing biological production. Net community production (NCP) over the upper 110 m, estimated from mass balances of salt, DIC, nitrate and nitrite (N+N), total organic carbon (TOC), and dissolved organic nitrogen (DON) was enhanced within the core of Cyclone *Opal* by a factor of 2-18 relative to surrounding waters. Most of the enhanced NCP appears to be stored in the surface waters as dissolved organic carbon (DOC) rather than exported as particulate organic carbon

(POC) to the deep ocean. Our results also indicate that the upper euphotic zone (0-75 m) is characterized by positive NCP and the lower layer (>75 m) is close to zero or net heterotrophic state. While the region surrounding the Hawaiian Islands was nominally identified as a CO_2 sink, mesoscale eddies may reduce the magnitude of the annual sink by more than 30% in the eddy-influenced region.

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M4: The myth of high nutrient content of prokaryotic heterotrophs in freshwater and marine systems: Does the evidence support the rhetoric?

Both the marine and freshwater literature is full of references to high nutrient content of prokaryotic heterotrophic microbes in these systems, yet few measurements of in situ nutrient content have been made, owing in part to measurement difficulties. Measurements in cultured organisms have been assumed to reflect the elemental composition of those in freshwater and marine systems. Most scientists assume that microbes have higher N and P content than the Redfield ratio (106 C:16 N:1 P by moles). We examined the elemental composition of prokaryotic heterotrophs in >100 lakes in the Upper Midwest (USA) though size-fractionation and found that bacterial N and P content (a) was not significantly greater than that of whole seston (unfractionated particles) and (b) was not significantly less than the Redfield ratio. A metadata analysis indicated a mean C:N:P of 245: 39: 1. These results indicate that heterotrophic bacteria may not necessarily be a disproportionately (relative to other food web components) important source of nutrients to higher trophic levels in lakes as suggested by the microbial loop hypothesis, either through direct trophic transfers or through nutrient regeneration. Comparisons of lake microbes with marine indicate more P in the marine organisms with a mean C: N: P of 63: 13: 1. However, nearly all of the marine measurements have been made with cultured microbes rather than in situ, so more measurements need to be made in marine systems.

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M5: Assessment of skill and portability in regional marine biogeochemical models: The role of multiple planktonic groups

Application of biogeochemical models to the study of marine ecosystems is pervasive; yet objective quantification of these models' performance is rare. Here, twelve lower trophic level models of varying complexity are objectively assessed in two distinct regions (equatorial Pacific and Arabian Sea). Each model was run within an identical 1-D physical framework. A consistent variational adjoint implementation assimilating chlorophyll-a, nitrate, export, and primary productivity was applied and

the same metrics were used to assess model skill. Experiments were performed in which data were assimilated from each site individually and from both sites simultaneously. A cross-validation experiment was also conducted whereby data were assimilated from one site, and the resulting optimal parameters were used to generate a simulation for the second site. When a single pelagic regime is considered, the simplest models fit the data as well as those with multiple phytoplankton functional groups. However, those with multiple phytoplankton functional groups produced lower misfits when the models are required to simulate both regimes using identical parameters were optimized, the models are required to a sonly a few key biogeochemical parameters were optimized, the models with greater phytoplankton complexity were generally more portable. Furthermore, models with multiple zooplankton compartments did not necessarily outperform models with single zooplankton compartments, even when zooplankton biomass data are assimilated. Finally, even when different models produced similar least squares model-data misfits, they often did so via very different element-flow pathways, highlighting the need for more comprehensive data sets that uniquely constrain these pathways.

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W21: Algal blooms in the Arabian Sea – Are they changing?

Until the late 90's, *Noctiluca miliaris* Suriray (synonym *Noctiluca scintillans* Macartney), a large heterotrophic dinoflagellate was a minor component of the phytoplankton population in the Arabian Sea, appearing in bloom form only sporadically in coastal regions predisposed to upwelling and deep slope water intrusions during the southwest monsoon. Since then however, *Noctiluca* blooms have increased in frequency and intensity, but with the majority of blooms being observed following the northeast monsoon season and at times, in association with the well known blooms of the diazotroph *Trichodesmium* sp. Microscopy and chemotaxonomy from HPLC analysis of phytoplankton pigments initiated in 2003 suggest that *Noctiluca* blooms are becoming more intense and widespread in the Arabian Sea. Large blooms of these organisms have also started appearing off the coast of Oman. This study uses the recently available merged SeaWiFS and MODIS/Aqua ocean color datasets to investigate the temporal evolution and spatial extent of these taxonomically validated blooms. Additionally, Aqua-MODIS SST and sea surface height anomaly data are used to investigate the role of mesoscale eddies in the production and dispersal of these blooms in the western north Arabian Sea.

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M6: Iron induced nutrient utilization in the high-nutrient low-chlorophyll regions: What makes the Southern Ocean different from the equatorial Pacific and North Pacific?

The perennially high-nutrient low-chlorophyll (HNLC) equatorial Pacific, North Pacific and Southern Ocean attracted oceanographers' attention in the early 1900s. In the last 15 years over a dozen iron enrichment experiments have unequivocally demonstrated that iron addition causes 10 to 20-fold

increases in chlorophyll, 5-15 fold increases in primary productivity and up to a 100 µmol drawdown in pCO2 in these regions. But is iron the chief reason for the persistently high nitrate concentrations in HNLC regions? In the North Pacific and the equatorial Pacific the answer seems to be yes. The SEEDS iron experiment in the North Pacific resulted in 19.2 mg m⁻³ surface concentrations of chlorophyll and ambient nitrate concentrations of 17 µM decreased to 2.8 µM 13 days after iron was added (Kudo et al., 2005). In the equatorial Pacific nitrate was drawdown from 11 to 5 µM in seven days (Coale *et al.*, 1996). But in the Southern Ocean the published results from six intentional iron additions and five natural iron addition experiments have consistently resulted in a relatively meager (< 30%) drawdown of nitrate. What makes the Southern Ocean different from the HNLC equatorial Pacific and North Pacific? With new knowledge from Southern Ocean iron enrichment experiments, we utilize a simple one-dimensional model to explore what makes the Southern Ocean different from the equatorial Pacific and the North Pacific. Here we will explore how iron, silicate, grazing, export, mixing and mixed layer depth determine the potential nitrate utilization during the Southern Ocean growing season. This model uses climatological physical data as a baseline and explores the possible biological response using simple ecosystem dynamic assumptions of mixing, loss and export. With our current knowledge of the light environment and iron regulation of the Southern Ocean we aim to diagnose what is ecologically possible if phytoplankton are relieved from iron limitation and if the light limitation of the Southern Ocean is less pronounced.

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M7: Model-derived estimates of primary production and carbon flux in the Ross Sea

A bio-optical production model that was forced with the simulated surface irradiance fields, corrected for cloud conditions, and a simulated underwater light field was used to estimate primary production and subsequent carbon flux at several sites in the Ross Sea. The fate of newly produced phytoplankton carbon obtained from simulations for the Ross Sea was investigated using budget calculations that included the effects of grazing, advection, and sinking. For the Ross Sea zonal advection is the dominant process controlling phytoplankton primary production carbon (up to 57%) in the outer-shelf regions in all seasons. Grazing is an important removal process in the summer in the inner- and mid-shelf areas of Ross Sea continental shelf waters, but was found to be less of a control relative to advective removal. Sinking is an important removal process, with 20% and 220% of the daily primary production being removed by this process in the summer and winter, respectively. Comparisons with similar calculations made for the western Antarctic Peninsula continental show differences in potential carbon pathways in the two systems.

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M8: Investigation of Microbial Influences on Dissolved Organic Matter Composition by Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

The role of the microbial web (phytoplankton, bacteria and protozoa) in the cycling of organic matter and nutrients has been well established in both freshwater and marine environments. It is generally accepted that the composition of dissolved organic matter (DOM) influences, and is influenced by, the number and type of microbes present in an aquatic environment. We now have complementary tools available to probe the molecular-level composition of DOM and the species-level composition of the microbial assemblage. We have combined these techniques to examine the changes in DOM composition as a function of microbial activity in a coastal marine environment, Vineyard Sound, MA. The composition of the microbial community was monitored with standard molecular-biology techniques while the molecular-level composition of DOM was ascertained with ultrahigh resolution electrospray ionization (ESI) Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometry. Here we present initial data on the composition of DOM within our microbial incubations and introduce the appropriate statistically-robust comparative techniques that will allow the development of hypotheses linking specific alterations and modifications within DOM to the presence and activity of particular groups of microbes.

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M9: Community structure, ballast, and POC profiles in the mesopelagic Twilight Zone

Many profiles of size-fractionated (<1 μ m, 1-51 μ m, >51 μ m) suspended particulate matter in the upper 1000 m have been collected in several biogeochemical ocean provinces using the Multiple Unit Large Volume in-situ Filtration System (MULVFS) and precursor systems over the past 30 years. Over 40 profiles have been analyzed for POC, CaCO₃, and biogenic silica concentrations. Using chemical and image analyses, we investigate in detail two sets of profiles taken from the Subantarctic (55°S, 172°W) and Antarctic (66°S, 172°W) zones of the Southern Ocean during the Southern Ocean Iron Experiment (SOFeX) in January-February 2002, and then examine the entire dataset for trends affecting the transfer efficiency of POC to depth.

POC is transferred to depth much more efficiently at 55°S in the Subantarctic than at 66°S in the Antarctic, with higher POC concentrations in all size fractions in the twilight zone (100-1000 m) at 55°S than at 66°S, despite up to an order of magnitude lower POC in surface waters at 55°S. Particles in the carbonate-producing 55°S did not have higher excess densities than particles from the diatom-dominated 66°S, indicating that there was no direct ballast effect that accounted for deeper POC penetration at 55°S. At 66°S, large (several mm long) fecal pellets were abundant from the surface to 150 m, but there was an almost total removal of large aggregates by 200 m. This points to the importance of particle loss rates from zooplankton grazing and remineralization as determining factors for the difference in twilight zone POC concentrations at 55°S and 66°S.

Whereas food web models such as Michaels and Silver (1988) predict that an abundance of large producers should lead to high export from the euphotic zone, we find that this trend does not propagate to depth, as the surface community of large phytoplankton at 66°S was associated with low POC levels in the twilight zone. In the entire 40+-profile dataset, we also find that communities with a high fraction of large surface biomass are weakly correlated with lower POC at depth. Further, we find no correlation between concentrations of ballast minerals and POC in the twilight zone, again suggesting that there is no direct ballast effect to account for POC penetration in the twilight zone. These analyses suggest that the rules governing surface export (e.g., phytoplankton size) and deep export (ballast minerals) do not necessarily apply to the mesopelagic.

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M10: Does assimilation of dissolved organic phosphorus support growth and export fluxes in the Sargasso Sea?

With dissolved inorganic phosphorus (DIP) concentrations ~10-fold lower than at the Hawaii Ocean Time-series (HOT), there is growing evidence that the Sargasso Sea is a phosphorus (P)-stressed ecosystem. Despite lower DIP concentrations, particulate phosphorus export fluxes in the Sargasso Sea are comparable to those measured at HOT. Moreover, elemental particulate flux ratios suggest that the material exported during the summer in the Sargasso Sea becomes increasingly P-rich relative to material exported in the winter. We show that high concentrations of dissolved organic phosphorus (DOP) and a winter to summer drawdown of ~2 mmol/m² within the euphotic zone is a sufficient source of phosphorus to support the observed phosphorus export flux over this period. Matching the seasonal DOP drawdown is a summertime euphotic zone alkaline phosphatase activity maximum. Additionally, turnover of DIP and DOP in the Sargasso Sea is rapid and microbially dominated. However, there are differences in P assimilation among the different taxonomic groups. We hypothesize that, at least seasonally, the DOP pool fuels phosphorus export from the Sargasso Sea, and suggest that DOP should be included as a primary autotrophic nutrient pool in marine biogeochemical models.

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M11: Coupling of sinking biogenic particulate fluxes and primary production in the euphotic zone of the Cariaco Basin, Venezuela

 CO_2 is drawn down from the atmosphere into the ocean through photosynthesis, generating biomass that sinks to the sea floor. Only 1% of the organic matter produced in the upper ocean reaches depths below 1500 m, due to dissolution and microbial degradation. Several studies have shown that the vertical flux of particulate organic carbon (POC) is strongly correlated to the settling rates of minerals like calcium carbonate, opal and lithogenic material, suggesting that they act as ballast and provide physical protection from degradation to POC. Results from the CARIACO (Carbon Retention in a Colored Ocean) time series program support this hypothesis. For over ten years, CARIACO has been studying the connections between primary production (PP) and the biogeochemical features of sinking particles in the Cariaco Basin, Venezuela, with moored sediment traps that collect settling matter at five depths between 125 and 1300 m, on a bi-weekly basis, for periods of six months. The geomorphology of this basin, which is a depression on the continental margin off the eastern coast of Venezuela, restricts deep water ventilation, making it anoxic below 250 m. Although the Cariaco Basin exhibits strong seasonal production cycles related to wind-driven upwelling, it has been observed that the flux of biogenic matter at all depths below the oxic-anoxic interface is not significantly correlated to primary production. In order to understand the flux of particles in the upper 100 m of the water column, deployments of drifting sediment traps in the Cariaco Basin have recently been carried out,

collecting settling material at 50 and 100 m. The hypothesis is that the flux of sinking material through the euphotic zone may be less affected by decomposition and dissolution than material reaching the deep moored traps. Initial results show significant differences in total carbon flux rates between these two depths. The following steps of this research include comparing shallow vs. deep sediment traps data, and examining potential connections between seasonal changes in surface chlorophyll *a* concentrations and vertical export of biogenic materials.

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M12: Impact of biological processes representation on global biogeochemical cycles in a 3-D ocean model

Biological models of various complexities are tested within a 3-D ocean model aimed at representing the main biogeochemical cycles. The biological configurations differ in the way they treat the phytoplankton compartment (from one to three types of phytoplankton), and by the nitrogen cycle, which is included in the latest version and not in the first. All biological configurations include dissolved and particulate organic matter, an implicit representation of zooplankton, together with the formation of biogenic silica, precipitation and dissolution of CaCO₃ shells. The performances of each biological model are assessed against available reconstructions and the effect of the various representations on the global biogeochemical cycles are examined. Further, sensitivity experiments to various biological parameters (growth, rain ratio, etc.) are performed.

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W15: Particle dynamics and biogeochemistry of the benthic nepheloid layer: Potential processes modulating POM delivery on the continental margin

Considerable evidence indicates that the benthic nepheloid layer (BNL) is a distinct environment where biologically and physically driven, particle-based geochemical transformations represent early diagenetic reactions that impact the balance between POC and PON remineralization and benthic delivery. Within the Gulf of Maine, the BNL extends to 30 m above the bottom and is a pervasive feature as evident in Gulf-wide particle beam attenuation transects. Tidal mixing and seasonal slope water inflow are believed to be responsible for BNL maintenance. Elevated concentrations of particulate organic matter, enhanced levels of oxygen consumption, extracellular enzyme activity, and greater biota abundance have been shown to be associated with the BNL as compared to overlying, relatively particle-free waters. Geochemical data from time-series sediment trap studies and optical measurements indicate a more organic-rich BNL particle environment than previously assumed, as well as a temporal relationship between suspended particle delivery to the BNL during seasonal phytoplankton blooms, a diverse community of BNL zooplankton consumers, and the importance of time-varying BNL resuspension fluxes to the transport and fate of toxic dinoflagellate cysts.

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M14: Potential contribution of fossil dissolved organic carbon from methane-bearing cold seeps to the deep open ocean

Vast reservoirs of gas hydrate in continental margin sediments have the potential to influence the properties of organic matter in both sediments and the overlying water column. Natural radiocarbon and stable carbon isotopes were utilized to determine if fossil methane-derived carbon associated with gas hydrate-bearing sediments was incorporated into the dissolved organic carbon (DOC) of both sediment pore waters and overlying near-bottom waters associated with cold seeps from the northern Cascadia margin offshore of Vancouver Island, British Columbia, Canada. Near the sulfate methane transition (SMT), where ¹³C-deplete methane is anaerobically oxidized, the δ^{13} C values of the DOC were also ¹³C-depleted. For example, pore water DOC from the SMT had a δ^{13} C of -60% at a site with a microbial methane source and -45‰ at a site with a thermogenic methane source, whereas DOC spatially separated from the SMT tended to reflect the δ^{13} C of the sediment organic carbon (-23 to -25‰). In both cases, methane-derived carbon was the predominant carbon source (80-100%) for DOC associated with the SMT. Moreover, ¹⁴C- and ¹³C-depleted bottom water DOC from the thermogenic gas hydrate site indicates that methane carbon constituted 30-50% of the bottom water DOC. Our results indicate that fossil-derived sources of carbon were a significant component of DOC in the pore waters and overlying water column of the cold seep systems we investigated. New studies further suggest that cold seeps (including mud volcanoes) along continental margins may be more prevalent than previously thought. Integrated fluxes of fossil DOC from cold seep systems, particularly those with high velocity fluid flow, may quantitatively contribute fossil methane-derived DOC to the aged DOC pools of the deep open ocean.

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M15: Biological controls of the CO₂ air-sea flux in a high latitude shelf sea (North Sea)

The carbon cycle of the North Sea, a Northwest European shelf sea, has been investigated using a three-dimensional coupled physical-biogeochemical ecosystem model. Simulations for the years 2001/2002 are thoroughly validated against high-resolution field data sets from the same period. The results indicate that the North Sea acts as a significant sink for atmospheric CO₂. The uptake of CO₂ is balanced by an export of carbon into the deep waters of the North Atlantic, confirming observations suggesting the efficient removal of CO₂ from the atmosphere via the continental shelf pump mechanism. The simulated net community production (NCP) and net primary production (NPP) reveal the biological controls of this transport: despite the higher NPP in the southern North Sea, NCP, i.e. net carbon fixation, and the NCP/NPP ratio are small because of high remineralization of organic matter in the continuously mixed water column. In contrast, in the surface layers of the northern North Sea, NCP, net carbon fixation and the NCP/NPP ratio are high because of the high export of organic matter into the deeper layer of the seasonally stratified system, preventing organic matter remineralization in the surface layer. The implementation of overflow production releasing semi-labile dissolved organic carbon under nutrient-limited conditions enables the model to reproduce the observed pCO₂ and DIC

drawdown during summer. This decoupling of carbon fixation from the control of nutrient uptake via a fixed C/N ratio is essential for a realistic simulation of the magnitude of the air-sea flux of CO_2 , and thus the carbon cycle of the North Sea.

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M16: Mechanisms for decoupling of the pycnocline, nitricline, and ferricline in the equatorial Pacific and their impacts on ecosystems

Measurements in the equatorial Pacific Ocean reveal that under the warm pool, the vertical structures of the pycnocline, the nitricline, and the ferricline have important first-order similarities. Sharp vertical gradients for all three fields are found in the depth range of approximately 120-200 meters. This depth horizon corresponds roughly to that of the time-mean position of the Equatorial Undercurrent (EUC) in the western Pacific, with the EUC being the main source of upwelling water in the east. It is clear that in many respects the processes that maintain the mean profiles of NO₃ and Fe (namely their sources and sinks) are independent of the processes controlling the density structure. For NO₃, the vertical profile reflects the integrated effect of photosynthesis and respiration over the large (decadal) inter-gyre exchange process. For Fe, it is thought that the profile is to first order determined by external sources of Fe, namely aeolian deposition along with river and sediment influxes along the coast of New Guinea.

Here it is proposed to test the hypothesis that for the equatorial Pacific, the biogeochemical response to variability in ocean circulation can result in the decoupling of the nitricline, the ferricline, and the pycnocline. For the case of Fe, the sediment sources along the coast of New Guinea are fixed relative to the vertical excursions of the pycnocline (and thereby the EUC), resulting in changes in Fe concentrations on isopycnal surfaces. For the case of NO₃, natural decadal variability in the ocean circulation is accompanied by changes in conditions in the extratropical source regions which can impact preformed nutrient concentrations, and as well as the inter-gyre transit time associated with changes in the overturning strength of the subtropical cells (STCs).

Importantly, such decoupling of bio-limiting nutrients can result in a nonlinear downstream ecosystem response in the upwelling region. This hypothesis finds support in the output of a state-of-the-art biogeochemical model embedded in an ocean circulation model, which has been forced with reanalysis fluxes over a period of 56 years. In response to an abrupt 34% change in equatorial wind stresses associated with the 1976/77 shift in the mean state of the Pacific as represented in NCEP, the model exhibits an abrupt 80% change in the surface Chl concentrations in the equatorial upwelling region (2°N-2°S, 150°W-90°W). This significant amplified response in Chl is reflected in a large-scale shift of 57% in the new production over the equatorial Pacific (180°W-90°W, 5°N-10°S). Through the evaluation of observations and model experiments, the goal will be to identify and evaluate the processes that can contribute to nonlinear responses in the equatorial Pacific ecosystems to changes in the physical climate system.

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M17: Estimating interannual climate variation impacts on abyssal macrofauna community dynamics in the NE Pacific

Life on the abyssal seafloor mediates carbon flux over much of the earth's surface, but our understanding of how seasonal and interannual scale climate variation alters deep-sea carbon budgets remains insufficient. Long-term studies at multiple deep-sea locations have demonstrated that benthic macrofauna in the deep-sea are known to respond to seasonal and pulsed inputs of particulate organic matter from sunlit surface waters. Utilizing *in situ* respirometry, benthic sediment samples, and sedimentation trap measurements we examined how such pelagic-benthic coupling varied interannually from 1989-1998 at a location 4,100 m deep in the NE Pacific. The results suggest that information on abyssal food supplies and surface conditions such as sea surface temperature, upwelling, and El Niño can be used to estimate benthic community dynamics at the study site.

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M18: Revisiting seasonal plankton cycles in the subarctic Atlantic and Pacific

Microscopic ocean phytoplankton play a vital role in the biogeochemical cycling of carbon and other essential elements, and their photosynthesis supports the largest contiguous ecosystem on earth. Carbon uptake by phytoplankton and the effectiveness of carbon sequestration to the deep ocean depend on phytoplankton biomass, growth rate, and ecosystem structure. Traditionally, phytoplankton biomass is quantified from chlorophyll measurements, both in the field and from satellite retrievals. This approach, however, ignores physiological variability in the chlorophyll content of phytoplankton cells, which acclimate to environmental conditions. Here we use two independent approaches, new satellite observations and a photo-acclimation model, to show that low chlorophyll concentrations in the eastern subarctic Pacific are the result of low cellular chlorophyll content, rather than of low phytoplankton biomass. Peak biomass concentrations are similar to the spring bloom regime of the North Atlantic, which contradicts the long-standing paradigm that environmental conditions prevent phytoplankton accumulation in the Northeast Pacific. Our findings challenge chlorophyll-based ecosystem studies and suggest that variable pigmentation should be taken into account when global estimates of carbon uptake and carbon sequestration are derived from satellite-observed chlorophyll.

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M19: Biotic control of sinking particle flux in the ocean's twilight zone

The downward flux of POC decreases significantly in the ocean's mesopelagic or 'twilight' zone due both to abiotic solubilization and fragmentation, and to biotic transformation and remineralization by resident microbes and zooplankton. The biological processes that mediate remineralization of POC into a dissolved form include solubilization by bacteria and consumption by zooplankton. During these processes particles also be may be fragmented, or repackaged into fecal pellets. However, the effect of microbial and zooplankton community structure on transformation or remineralization of particles in the mesopelagic zone is not well known. We characterized the mesopelagic microbial and zooplankton community, and sinking particle flux, at the Hawaii Ocean Time series (HOT) station ALOHA in the subtropical Pacific and the Japanese times series site (K2) in the subarctic Pacific to determine the potential contribution of the biota to processing of sinking POC. We estimated the contribution of mesopelagic bacteria and zooplankton to remineralization of sinking particles by comparing losses of sinking C measured by sediment traps with bacteria and zooplankton metabolic requirements. We further investigated how zooplankton fecal pellet characteristics changed with depth in order to quantify the extent of particle repackaging by zooplankton. Bacteria carbon demand exceeded that of zooplankton at ALOHA, while bacteria and zooplankton required relatively equal amounts of POC at K2. However, sinking POC flux was inadequate to meet metabolic demands at either site. We suggest diel vertical migration plus carnivory supports a greater fraction of mesopelagic carbon demand than does sinking POC. We also saw significant changes in types of zooplankton fecal pellets with depth at both sites, indicative of midwater consumption and repackaging of sinking particles. These include changes in flux of larvacean, large copepod, and carnivore fecal pellets with depth. These results will help incorporate the roles of both bacteria and zooplankton in predictive biogeochemical models, and have important implications for models of C export and sequestration in the deep sea.

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W1: Stable carbon isotope discrimination by form IC Rubisco enzymes of the extremely metabolically versatile *Rhodobacter sphaeroides* and *Ralstonia eutropha*

Variations in the relative amounts of ¹²C and ¹³C in microbial biomass can be used to infer the pathway(s) autotrophs use to fix and assimilate dissolved inorganic carbon. Discrimination against ¹³C by the enzymes catalyzing autotrophic carbon fixation is a major factor dictating biomass stable carbon isotopic compositions ($\delta^{13}C = \{[^{13}C/^{12}C_{sample}/^{13}C/^{12}C_{standard}] - 1\} X 1000$). Five different forms of RubisCO (IA, IB, IC, ID, and II) are utilized by algae and autotrophic bacteria reliant on the Calvin-Benson cycle for carbon fixation. To date, isotope discrimination has been measured for form IA, IB, and II RubisCOs, and their ε values (= $\{[^{12}k/^{13}k] - 1\} X 1000$; ¹²k and ¹³k = rates of ¹²C and ¹³C fixation) range from 18 to 29‰, explaining the variation in biomass $\delta^{13}C$ values of autotrophs utilizing these enzymes. Isotope discrimination by form IC RubisCO has not been measured, despite the presence of this enzyme in many proteobacteria of ecological interest, including marine manganese-oxidizing bacteria, some nitrifying and nitrogen-fixing bacteria, and extremely metabolically versatile organisms such as *Rhodobacter sphaeroides* and *Ralstonia eutropha*. The purpose of this work was to determine the ε values for form IC RubisCO enzymes from *R. sphaeroides* and *R. eutropha*. Recombinant form IC RubisCOs were purified by conventional column chromatography procedures. Assay conditions (pH and dissolved inorganic carbon concentration) were tested to determine which

parameters were conducive to the high rates of carbon fixation necessary for ε determination. Under standard conditions (pH 7.5 and 5 mM DIC), form IC RubisCO activities were sufficient for ε determination. Experiments are currently being conducted to measure the ε values of these enzymes. Sampling the full phylogenetic breadth of RubisCO enzymes for isotopic discrimination makes it possible to constrain the range of δ^{13} C values of organisms fixing carbon via the Calvin-Benson cycle. These results are critical for determining the degree to which Calvin cycle carbon fixation contributes to primary and secondary productivity in microbially dominated food webs.

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M20: Nitrogen uptake and regeneration pathways in the equatorial Pacific

Marked deep maxima of ammonium (DAM) and nitrite (DNM) have been widely observed in the lower euphotic zone of the equatorial Pacific, showing an asymmetric feature with a stronger deep maximum in the south of the equator than in the north. Both DAM and DNM are net products of sink (nitrogen uptake by phytoplankton) and source (zooplankton excretion, and remineralization of dissolved organic nitrogen (DON) and detritus). A fully coupled 3-dimensional physical-biogeochemical model is applied to study the nitrogen cycle, focusing on uptake and regeneration pathways in the tropical Pacific ecosystem. Two sets of observation data (Libby and Wheeler, 1997; Raimbault et al., 1999) are used for model validations and improvements.

The model simulates large and small sizes of phytoplankton, zooplankton, and detritus, DON, nitrate, and regenerated nitrogen. The model can reproduce many observed features in nitrogen fields, including the asymmetric distribution of DON, nitrate, and regenerated nitrogen. Our study shows that zooplankton excretion and DON remineralization play different roles in generating nutrients over space and time, demonstrating the need for including these processes in biogeochemical models.

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M21: Analysis of *rbcL* gene sequence diversity and mRNA levels in the Gulf of Mexico: Contribution of chlorophytes to the eukaryotic autotrophic picoplankton

Autotrophic marine picoplankton are composed of *Synechococcus*, *Prochlorococcus* and a diverse array of small eukaryotic algae. The eukaryotic component of the autotrophic picoplankton is the least well studied of the three and picoeukaryote diversity, distribution, and their individual contributions to productivity are not yet well understood. Two major lineages of picophytoplankton, the "green" and the "golden-brown" lineages, exist in the oceans. The "green" lineage includes the division Chlorophyta, while the "golden-brown" lineage is composed of haptophytes (prymnesiophytes including coccolithophorids) and stramenopiles (heterokont algae including diatoms and pelagophytes). Traditionally, the chlorophytes have not been considered to be an important component of the autotrophic marine picoplankton. We evaluated this notion by analyzing species diversity and carbon fixation gene expression during two cruises in the Gulf of Mexico via quantification and cloning of *rbcL* (large subunit gene of RubisC/O, the key enzyme in the Calvin cycle) mRNA

transcript. The green and golden-brown linages can be distinguished because they contain different forms of the *rbcL* gene (Form IB and ID, respectively). Form ID *rbcL* mRNA was dominant in the upper euphotic zone of the central, oligotrophic Gulf of Mexico, where no chlorophyte *rbcL* mRNA was detected. Chlorophyte *rbcL* mRNA accounted for >80% of the total eukaryotic *rbcL* mRNA signal at the SCM (subsurface chlorophyll maximum), however. Chlorophyte *rbcL* mRNA was found throughout the water column at a station that was influenced by the Mississippi River Plume, where it was the dominant form of transcript in samples collected at depths between the surface plume and the SCM. *rbcL* mRNA analysis along a transect of the Mississippi River Plume (onshore to offshore) indicated that chlorophytes accounted for 25-40% of the total eukaryotic *rbcL* signal in the plume. Similarly, 20-30% of all eukaryotic *rbcL* phylotypes detected along this transect were of the Form IB type. Phylogenetic analysis indicated that prasinophytes (a class of algae within the division Chlorophyta) are found mainly at the SCM, while other green algae can be found throughout the water column, particularly where the Mississippi River plume influences productivity. These data suggest that chlorophytes may be a hitherto underappreciated component of the eukaryotic, autotrophic picoplankton in the subtropical coastal oceans. Further work is needed to determine chlorophyte abundance, diversity, and distribution.

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M22: A modeling study of developmental stage and environmental variability effects on copepod foraging

A stochastic, object-oriented Lagrangian model is used to study how behavior contributes to copepod grazing success. The model simulates distinct foraging behaviors of *Clausocalanus furcatus*, *Paracalanus aculeatus*, and *Oithona plumifera*. Three sets of simulations were performed to investigate the effects of: 1) prey size preference; 2) variation in prey size spectra; and 3) turbulent intensity on these species' grazing rates. The size preference simulations show that compared to copepodites, mature females have cell ingestion rates that are an order of magnitude lower while carbon uptake is reduced by 35%. A prey spectrum skewed toward cells < 6 µm promotes copepodite success since the basal metabolic needs of the adult females require a prey concentration of 850 to 1000 cells ml⁻¹. The turbulent intensity simulations promote spatial variability in species distribution, with *O. plumifera* preferring stronger mixing and *C. furcatus* better suited to stable conditions. Differences in theoretically derived and simulated prey encounter rates show that the hopping behavior of *O. plumifera* provides an order of magnitude increase in prey encounter while the feeding behavior of C. furcatus can result in localized depletion of prey. These simulations highlight the importance of species-specific feeding behavior in defining oceanic copepod distributions.

THEME 2. CHANGING OCEAN BIOGEOCHEMISTRY: THE PREDICTION CHALLENGE

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T1: Long-term physical, chemical and biological measurements in the Southern California Current: Establishing the context for natural and anthropogenic change

The complex interplay between the various modes of natural climate forcing significantly challenges our ability to predict the upper ocean's response to global warming and ocean acidification. Physical and biogeochemical data collected as part of long-term time series observations allow a retrospective assessment of the mechanisms of change and establish a framework for interpretation of synoptic observations. The California Cooperative Oceanic Fisheries Investigations (CalCOFI) survey has been providing physical, chemical and biological data for the southern California Current System since 1949; the time series constitute an ideal data set to help disentangle natural variability on the interannual and decadal scales from any possible long term trends. The CalCOFI observations are centered on the productive biome sustained by coastal upwelling. The high frequency forcing of El Niño and La Niña events as well as the lower frequency forcing associated with the Pacific Decadal Oscillation (PDO) is manifested strongly in matrix of variables. This forcing provides an ideal platform and a number of useful "case studies" for examining biophysical coupling. In this context, a new Long Term Ecological Research (LTER) site was established within the CalCOFI domain to examine the biogeochemical and physical consequences of these natural perturbations as well as the consequences of any long-term secular warming trend.

In this presentation we briefly highlight some of the recently published studies that have identified both interannual and decadal scale variations in physical parameters (such as surface ocean temperature, depth of the thermocline and wind stress) and biological parameters (such as zooplankton stocks). In addition, we present new data examining the nitrogen and phosphorus dynamics of the California Current system; the analysis explores the expression of climatic forcing on the inventory and source of nutrients in surface waters of the CalCOFI region. Finally, we will describe some of the newer biogeochemical tracers that have recently been added to the CalCOFI domain.

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T2: Particle settling velocities from settling-velocity traps in MedFlux agree with those from time-series sediment traps both in MedFlux and elsewhere: They average 300-400 m/d

A central focus of MedFlux research has developed around the use of Indented Rotating Sphere (IRS) sediment traps in "settling velocity" (SV) mode. These traps sort particles into settling velocity classes, enabling flux estimates and chemical analyses of particles as functions of settling velocity. We estimated settling velocities for eight deployments of these traps in 2003 and 2005. In each case we determined the most likely sinking velocity (the "modal" velocity); the estimated modal settling velocities of "fast settling" particles are 300-500 m/d, with average value 331 m/d. This value is 2-4 times higher than the "canonical" value 80-200 m/d. Because these results differ so greatly from delivered wisdom, they have been greeted with skepticism by some in the oceanographic community.

In response to this skepticism, a new method was developed for improving the sensitivity of the standard "benchmark" approach, which estimates settling velocity from the time-of-flight of particles between pairs of traps at different depths. This new method, based on fitting Fourier series to time-series data, was applied to data from MedFlux and from the US JGOFS NABE, EqPac, and ASPS studies. Fluxes of a variety of tracers were plotted on linear scales, on logarithmic scales, and as molar ratios, and were fit using this new method. We estimated sinking velocities between 26 pairs of traps,

in each case making 5 estimates using different tracers. Our results showed no significant differences among SV's estimated using different tracers. There were, however, large differences between SV's estimated using single tracers and those estimated using ratios of tracers; we argue that single tracers give more reliable results. Modal settling velocities estimated using log-transformed fluxes for openocean sites with good temporal resolution (i.e, for sites having cup rotation times ≤ 8.5 days) are in the range 77-966 m/day, with average modal value 330 m/day.

We also discuss why, in retrospect, these results should not have been surprising. In particular, settling velocities larger than 200 m/d have long been known. The present results are also not inconsistent with a more recent implementation of the "benchmark" approach by Berelson (2002), because his estimates of 80-330 m/d (already extending upwards of 200 m/d) were biased towards giving settling velocities that are too low.

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T3: Decadal variability in the biogeochemistry of North Atlantic mode waters

Mode waters are important reservoirs for carbon and nutrients. Time-series studies and repeat hydrographic surveys suggest that waters at intermediate depth exhibit large variability in physical and biogeochemical quantities on multi-annual to decadal timescales. An understanding of the temporal and spatial characteristics of this variability and of the quantitative and mechanistic aspects of the underlying dynamics is critical for predicting the future development of the global oceanic carbon and nutrient cycles. We here present results from model runs with the ocean component of the NCAR CCSM climate model with an embedded multi-functional group ocean biogeochemistry model (FGM) that is forced at the surface by historical atmospheric conditions. We explore the computed variability in North Atlantic mode water formation and spreading and its role for the interannual to decadal accumulation and release of nutrients and carbon. We use O_2 and other model tracers to identify changes in variability due to biology, circulation and ventilation. The observed variability in Subtropical Mode Water (STMW) appears to be driven mostly by circulation changes, contraction and expansion, slowing and acceleration of the subtropical gyre, while ventilation (defined here as an increase in the flux of O_2 -rich waters from the surface ocean into the thermocline) and biology are only of secondary importance.

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T4: Toward an improved understanding of air-sea exchange of gaseous organic carbon and its role in ocean carbon fluxes

Atmospheric deposition has long been recognized as an important source of allochthonous nitrogen, various trace elements, and specific organic compounds to the oceans. However, at present the magnitude and forms of total atmospheric organic carbon (OC) inputs to the oceans are essentially unknown, although recent reports suggest that large atmospheric inputs of biologically reactive OC may be sufficient to account for the observed net heterotrophic activity of the subtropical northeast Atlantic and other remote marine systems. Moreover, the contribution of anthropogenic emissions of

fossil fuel-derived OC to the present-day atmosphere may represent a significant influx of pre-aged OC to the oceans.

Air-sea gas exchange of OC has recently been recognized as a potential source of global significance to ocean waters. Based on currently available data, we calculate that gas deposition of OC to the oceans is more than an order of magnitude higher than wet and dry atmospheric deposition fluxes, and that atmospheric inputs may supply as much as 2-3 times more OC to the oceans than riverine inputs. Nonetheless, our estimates of OC gas deposition to the northwest Atlantic Ocean are ~30 times *lower* than those recently reported for the northeast Atlantic Ocean, thus illustrating *i*) the potential and substantial spatial and/or temporal variability in atmospheric deposition fluxes of OC to the oceans, and/or *ii*) significant differences in experimental and/or computational techniques for determining air-sea gas deposition fluxes of OC. We suggest that the OC gas fluxes recently determined for the northeast Atlantic Ocean may be overestimates due in part to inadequate differentiation between volatile organic carbon (VOC), semi-volatile organic carbon (SVOC), and water-soluble volatile organic carbon (WSVOC) in air and seawater. We further propose that in order to accurately quantify air-sea gas exchange of the diverse pool of atmospheric OC, it is critical to distinguish gaseous OC according to its physical-chemical properties and the dominant film resistance(s) to mass transfer.

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T5: Ocean acidification of the greater Caribbean region 1996 – 2006

Human activities have driven atmospheric carbon dioxide (CO₂) concentrations to levels greater than, and increasing at a rate faster than, experienced on Earth for at least the last 650,000 years. Global oceans are the largest natural reservoir for this excess CO₂, absorbing one-third of that emitted each year. Rising levels of CO₂ are changing ocean chemistry more dramatically than in over 20 million years. As CO₂ reacts with seawater, fundamental chemical changes occur that cause a reduction in seawater pH (or acidification) and reduce the availability of chemical compounds that play an important role in shell creation for a number of marine organisms. Ocean acidification (OA) could affect some of the most fundamental biological and geochemical processes of the sea in coming decades. We will estimate the change in sea surface chemistry that has transpired over the past decade throughout the Greater Caribbean Region (GCR) as a consequence of ocean acidification. Improved parameterization of satellite-derived carbon dioxide partial pressure $(pCO_{2 sw})$ fields for the GCR have been obtained using empirical relationships derived from shipboard pCO_{2,sw}, sea surface temperature (SST), and salinity measurements taken aboard the Explorer of the Seas operated by the Royal Caribbean International. The model is constrained using NOAA OI SST and estimates of atmospheric pCO_2 ($pCO_{2,air}$). The $pCO_{2,air}$ is computed from dry atmospheric CO₂ mole fraction data (XCO₂) obtained from the NOAA/CMDL carbon Cycle Greenhouse Gases Group flask sampling program and gridded fields of daily mean sea level pressure (SLP) obtained from the NOAA-CIRES Climate Diagnostics Center. Comparisons between shipboard measurements and co-located model estimates indicate that the present model accounts for ~75% of the variability and exhibits an RMS of $\pm 10 \mu atm$. Empirical relationships of total alkalinity (A_T) with salinity and temperature in surface waters were recently offered by Lee et al. (2006). We will apply these relations to estimate surface alkalinity in the GCR from 1996-2006 and couple them to corresponding pCO_{2sw} fields. Pairing A_T and pCO_{2,sw} will

then permit us to characterize the changes in sea surface carbonate chemistry as a consequence of ocean acidification over this period. This research contributes toward the goals of major U.S. Climate Change Science Program (CCSP) activities, including the U.S. North American Carbon Program (NACP), the Ocean Carbon and Climate Change Program (OCCC) and the Ocean Biogeochemistry Program (OCB).

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W19: SIBER: Sustained Indian Ocean Biogeochemical and Ecological Research

There are many outstanding research questions in the Indian Ocean because it is a dynamically complex and highly variable system, yet it is substantially under-sampled compared to the Atlantic and Pacific. The unique physical dynamics of the Indian Ocean arise largely as a result of the Eurasian land boundary to the north, which, among other things, gives rise to the strong seasonally reversing monsoon winds. These winds drive intense upwelling and downwelling circulations and seasonally reversing surface current patterns. These, in turn, give rise to substantial variations in marine biogeochemical and ecosystem response.

Due to this complexity we still do not have a complete characterization and understanding of the primary production variability and dynamics in the Indian Ocean. Nor have the impacts of major physical perturbations, associated with phenomena like the Madden-Julian Oscillation and the Indian Ocean Dipole, been characterized. This is in marked contrast to the Atlantic and Pacific where the seasonal blooms dynamics are relatively well described and understood, and also the impacts of interannual influences such as NAO and ENSO. Questions also persist about the role of the Indian Ocean in the global carbon and nitrogen cycles, and about the role of grazing versus nutrient limitation in mediating primary production and bloom dynamics in the Arabian Sea. Furthermore, there is exciting emerging evidence which suggests that Fe limitation may be important in the Indian Ocean and even in the Arabian Sea during the southwest monsoon. However, direct measurements and experiments are limited. Global warming impacts are also becoming apparent in the Indian Ocean, such as the emerging evidence that climate change is influencing the strength of the monsoon winds, and also the rapid warming of the Indian Ocean surface waters, both of which could have profound impacts on biogeochemical and ecosystem dynamics.

In response to broad international interest, collaborators from the U.S. and India convened the SIBER (Sustained Indian Ocean Biogeochemical and Ecological Research) workshop in Goa, India, during October 3-6, 2006. The event, hosted by India's National Institute of Oceanography (NIO), consisted of 4 days of presentations, posters and working group discussions (see http://ian.umces.edu/siber). The overarching goals of the workshop were to review the state of our knowledge of the biogeochemical and ecological dynamics of the Indian Ocean and define the major scientific questions that need to be addressed in order to formulate a plan for future international research in the IO in conjunction with the planned CLIVAR/GOOS Indian Ocean mooring array.

The SIBER workshop was an overwhelming success, with participation by over 200 scientists from all over the world. There was a clear consensus among workshop attendees that a new international research program needs to be motivated in the Indian Ocean under the auspices of OCB, IMBER, and

GOOS.

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T6: The impact of changes in the ocean's biological pump on atmospheric CO₂

Changes in the ocean's biological pump can have a substantial impact on the atmosphere-ocean balance of CO₂, yet the magnitude of the response in this balance to a given change in the vertical export of organic carbon and CaCO₃, i.e., the atmospheric uptake efficiency, is not well understood. We investigate here the factors that determine the atmospheric uptake efficiency on the basis of a suite of iron fertilization experiments using a coupled physical/biogeochemical/ecological model of the Pacific Ocean at an eddy-permitting resolution. We conduct our iron fertilization experiments primarily in the eastern tropical Pacific, and vary them in size from a very small patch with a size of the order of a few thousand square kilometers to the entire Pacific. While our standard procedure entails continuous fertilization with iron for 10 years, we also considered cases where the fertilization is undertaken over only a few months. For the patch size-scale experiments (less than 106 km²), we find relatively high atmospheric uptake efficiencies over 10 years (order of 0.75 to 0.9), which means that between 75% and 90% of the carbon that is exported across 100 m depth comes from the atmosphere. This efficiency is insensitive to the duration of the experiment, but tends to decrease with increasing size of the fertilized region. We identify the vertical distribution of the changes in the biological pump within the euphotic zone as the primary factor controlling the atmospheric uptake efficiency. The closer to the surface the biological pump is stimulated, the more efficient it is in taking up CO₂ from the atmosphere. Therefore, iron fertilization, which tends to induce a surface enhanced bloom of phytoplankton, tends to have much higher atmospheric uptake efficiencies than previous nutrient restoring-based experiments where most of the enhanced export came from the lower parts of the euphotic zone. The importance of the depth distribution for controlling the atmospheric uptake efficiency arises from the competition of the different pathways for resupplying the dissolved inorganic carbon that has been taken up by phytoplankton and exported to depth. Near the surface, most of this carbon comes from the atmosphere, whereas in the lower parts of the euphotic zone, most of this carbon is supplied laterally and from below. The dependence of the atmospheric uptake efficiency on the vertical distribution of the changes in the biological pump is relevant for understanding the impact on atmospheric CO₂ of any changes in this pump, irrespective of whether they are induced by iron or other factors, such as climate change.

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T7: Annual carbon productivity in the Southern Ocean: Revisiting the Martin Iron Hypothesis

Martin's (1990) Iron Hypothesis proposed a mechanism whereby iron availability in the Southern Ocean could regulate global atmospheric CO₂ concentrations during glacial and interglacial periods.

Southern Ocean iron enrichment experiments have now unambiguously demonstrated a key Martin tenet: the proximate role of iron availability in increasing primary production and carbon export. Results from the mid-summer 2002 iron addition experiment conducted in the Pacific sector of the Southern Ocean in the high nitrate, high silicic acid, low chlorophyll waters poleward of the southern boundary of the Antarctic Circumpolar Current (66°S, 172°W) together with earlier process study observations in the same region were used to calculate annual primary production, annual new production and annual carbon export in context with seasonal light availability and ice coverage for present-day iron-limited conditions and for hypothetical year-round iron-replete conditions. We calculated that iron-enrichment could increase annual primary production by about 2.3-fold (from 6.1 to 14.3 mol C m⁻² y⁻¹) and new production by about 5-fold (from 1.6 to 7.9 mol C m⁻² y⁻¹). Calculated annual iron-enriched carbon export ranged from ~ 3 to ~ 10 mol C m⁻² y⁻¹ depending upon hypothesized annual export ratio scenarios developed from a limited number of observations. The ultimate fate of iron-enriched primary production remains almost as puzzling today as when Martin troubled over the lack of evidence for increased production in the sedimentary record. Although progress is being made, our understanding of the linkage between Southern Ocean iron availability, primary productivity and carbon export from the surface ocean is far from complete. Consequently, the impact of iron addition to the surface ocean on drawdown of global atmospheric CO₂ has yet to be resolved.

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T8: Particulate organic matter and ballast fluxes measured using Time-Series and Settling Velocity sediment traps in the northwestern Mediterranean Sea lead to new ideas on particle export

Prompted by recent data analyses suggesting that the flux of particulate organic carbon sinking into deep waters is determined by fluxes of mineral ballasts, we undertook a study of the relationships among organic matter (OM), calcium carbonate, opal, lithogenic material, and excess aluminum fluxes as part of the MedFlux project. We measured fluxes of particulate components during Spring and Summer of 2003 and 2005 using a swimmer-excluding sediment trap design capable of measuring fluxes both in a time-series (TS) mode and in a configuration for obtaining particle settling velocity (SV) profiles. On the basis of these studies, we suggest that distinct OM-ballast associations observed in particles sinking at a depth of ~ 200 m imply that the ratio of organic matter to ballast is set in the upper water column and the importance of different ballast types follows the seasonal succession of phytoplankton. Dust appears to increase particle flux through its role in aggregation rather than in nutrient input that enhances productivity. Particles must be at least half organic matter before their settling velocity is affected by ballast concentration. This lack of change in ballast composition with SV in particles with <40% OM content suggests that particle SV reaches a maximum because of the increasing importance of inertial drag. As expected, relative amounts of OM and opal decrease with depth due to decomposition and dissolution; carbonates and lithogenic material contribute about the same amount to total mass, or increase slightly, throughout the water column. The high proportion of excess Al cannot be explained by its incorporation into diatom opal or reverse weathering, so Al is most likely adsorbed to particulate oxides.

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T9: Characterization of sinking particles using advanced solid-state NMR

Sinking particles are the major vehicle for transporting organic carbon from surface to the deep ocean, and their chemical composition changes dramatically as they sink through the water column. However, the exact mechanism controlling the chemical transformation is not well understood, mainly due to the paucity of techniques to analyze the major macromolecular components of the organic matter of sinking particles. In this study, we applied advanced NMR techniques including CPMAS, 2D HETCOR and T₁ inversion recovery on the sinking particles collected at the DYFAMED site in the Mediterranean Sea (MedFlux). Our preliminary results show that particles from 200 m with different sinking velocities have a similar chemical composition, suggesting that mineral content and/or particle size is important in controlling the sinking velocity but not organic matter composition. The major classes of chemical compounds identified included lipids, carbohydrate and proteins, consistent with the results from routine chromatographic analysis. The NMR results on sinking particles from 200, 520 and 920 m were compared, and the data indicate that the macromolecular heterogeneity observed in surface particles virtually disappears with increasing depth. This suggests that the macromolecular components at depth are not similar in structural composition to those in surface waters.

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T10: Decadal variability of temperature, salinity, oxygen, inorganic nitrogen, phosphorus and carbon in the Mediterranean Sea

We took advantage of the release of a new database for the Mediterranean Sea (Medatlas, 2002) to constitute several sets of monthly climatologies over the 1958–1999 time period. These climatologies allow us to analyze the variability of temperature, salinity and the N, P, O₂ parameters in the Mediterranean Sea. Decadal variabilities of temperature and salinity are closely related to those found in air-sea heat fluxes and, in some part of the Mediterranean Sea it seems to be partly correlated to climate anomalies (such as North Atlantic Oscillation). Nutrient, oxygen and phosphorus annual cycles allow us to estimate the carbon export from the mixed layer and the shallow mineralization. Results show that the carbon export has reached a maximum during the eighties in the southern part of the basin and this is confirmed by higher averages of chlorophyll content during this time period. In the northern part of the sea, the carbon export tends to increase with time, which might be related to an increase of terrestrial discharge by the rivers. We use indirect methods based on our climatologies to reconstruct 40 years of sea surface carbon dioxide. The Mediterranean Sea is a net source of CO₂ for the atmosphere, and this source tends to decrease with time. There is no evidence from our data that SST has been increasing over these 4 decades in the Mediterranean Sea.

changes in SST and SSS in the areas of deep water formation confirm the shift already reported about a deep water formation that has been more important in the Crete Sea during the nineties than in the North Adriatic, which has led to a change in the Mediterranean water circulation. The consequences for the biogeochemical cycles of C, N, P, O₂ are discussed in the light of the trends we found in our climatologies with respect to the uncertainties.

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T11: Paleo-JGOFS: A case study in the central equatorial Pacific based on uranium isotope compositions in foraminiferal tests from sediments

Prediction of the ocean acidification and/or ocean's capability for storage of anthropogenic CO_2 requires thorough understanding of the mechanisms controlling the ocean carbon cycle. One way to acquire such understanding is by looking into the changes of carbon cycle in the paleo-ocean in association with the past changes of CO_2 concentration in the atmosphere. Being capable of forming stable uranyl-carbonate complexes in sea water, uranium isotopes in foraminiferal tests are found to be a potentially useful proxy for constraining the $CO_3^{=}$ chemistry in paleo-seawater. We report here measurements of U/Ca and ²³⁴U/²³⁸U ratios in foraminiferal microfossil calcite tests from a 500-kyr central equatorial Pacific sediment core P-72 by using inductively coupled plasma-mass spectrometry (ICP-MS). The results show that for the last several glacial/interglacial cycles, the foraminiferal U/Ca ratios in core P-72 are higher during the interglacial times than during the glacial times and are inversely correlated with the ${}^{234}U/{}^{238}U$ ratios in the tests. Such correlation indicates a significant increase of the surface-ocean productivity and a significant drawdown of the surface-water pCO_2 in the central equatorial Pacific during the glacial times, providing important evidence showing that the decreases of the glacial surface-water pCO_2 in the central equatorial Pacific are in phase with those of the atmospheric pCO_2 , and such decreases are likely to be driven by the increased ocean productivity in the area. A quantitative estimate from the observed foraminiferal U/Ca ratios further suggests that while the central equatorial Pacific is today an important source of CO₂ to the atmosphere, such equatorial CO₂ source has been shut off during most of the glacial times and this glacial shut-off may contribute significantly to the drawdown of the glacial atmospheric pCO_2 .

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T12: PIC/POC flux response to CaCO₃ saturation state: field verification of the feedback on ocean acidification and CO₂

Recent work (*e.g.*, Riebesell et al., 2001; Zondervan et al., 2002) has suggested that the rate of planktonic calcium carbonate formation responds to the degree of supersaturation (Ω), with lower Ω resulting in lower particulate inorganic carbon (PIC) production and subsequently lower PIC to particulate organic carbon (POC) ratios. As the formation of PIC results in release of CO₂ into the surface ocean/atmosphere, lower PIC/POC ratios in sinking particulate matter in the ocean directly enhance the strength of the biological pump at sequestering carbon below the oceanic thermocline on

relatively short timescales (<1000 years) and diminish the impact of invading anthropogenic CO_2 on ocean pH (e.g., Zondervan et al., 2002).

We present a compilation of sediment trap data and estimated/measured Ω values that support the hypothesis that decreased Ω results in less PIC production and lower PIC/POC ratios. We then use this information, along with stoichiometric information from Zondervan et al., and other sources to scale up this observation to the global/regional scale in order to make predictions regarding the strength of this negative feedback to rising CO₂.

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T13: CO₂ flux variability in the North Atlantic: The impact of the spring bloom

Prediction of future change in ocean carbon uptake requires better understanding of current flux variability and its relationship to ecosystem processes. The North Atlantic is of particular interest because it is region of large net sink (Sabine et al. 2004). Atmospheric inversions employing the standard large-region approach (Baker et al. 2006) suggest relatively large flux changes from year to year for this region, while forward models and small-region inversions (Rodenbeck et al. 2003, McKinley et al. 2004) suggest only small variability. The region clearly warrants additional attention. We are studying recent variability in air-sea CO₂ fluxes using a moderately high resolution (0.5°) North Atlantic model that incorporates the ecosystem model of Dutkiewicz et al. (2005) and carbon cycling. The seasonal cycle of the surface ocean pCO₂ is in close agreement with the data of Takahashi et al. (2002). Consistent with previous models, we find small basin-integrated year-to-year flux variability, but local variations are large, particularly where and when the spring bloom is strong. In this poster, we present our emerging understanding of the relationship between bloom variability and CO₂ flux changes.

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T14: Decadal variability in the North Pacific thermocline diagnosed from oxygen measurements: Results from the U.S. CLIVAR/CO₂ Repeat Hydrography cruises

The data collected during the CLIVAR/CO₂ Repeat Hydrography Program have been giving new information regarding climate variability throughout the water column. Here, the focus is on the data collected on the two U.S. North Pacific CLIVAR/CO₂ cruises, P2 and P16N, which provide (among other properties) new high quality oxygen measurements useful for further study of thermocline variability in the North Pacific. These two repeat cruises were conducted along 30°N in 2004 and 152°W in 2006 following the cruise tracks of the corresponding WOCE cruises in 1994 and 1991, respectively. For the analysis of the data, oxygen concentrations are converted to apparent oxygen utilization (AOU = oxygen concentration in equilibrium with the atmosphere - measured oxygen concentration), which describes the amount of oxygen consumed due to respiration since a water

parcel has left the mixed layer. In the upper water column, large increases in AOU concentrations between WOCE and CLIVAR/CO₂ are observed along P2 as well as P16N. The increases are most prominent in the eastern portion of P2 ($\leq 170^{\circ}$ W) and the northern portion of P16N ($\geq 30^{\circ}$ N) where AOU differences exceed 20 µmol kg⁻¹ at the same core density (σ_{θ} =26.6 kg m⁻³) as in previous studies. In contrast, comparison of CLIVAR/CO₂ P16N with an additional cruise along 152°W in 1997 indicates that from 1997 to 2006 AOU concentrations on σ_{θ} =26.6 kg m⁻³ have decreased at the subtropical-subpolar gyre boundary. This reversal in the sign of the AOU differences suggests that AOU anomalies are moving through the North Pacific thermocline as pulses with decadal time scales.

Past simulations with the Hallberg Isopycnal Model as well as analysis of chlorofluorocarbon age data in conjunction with AOU data have confirmed that most of the observed AOU changes in the North Pacific must be due to physical processes rather than changes in biology. Studies of longer term oxygen variability at Ocean Station P in the eastern subpolar North Pacific and in other parts of the subpolar gyre have also found ventilation changes on decadal time scales. The CLIVAR/CO₂ observations will be discussed in the context of these studies. Potential forcing mechanisms for the observed AOU variability, such as the Pacific Decadal Oscillation and the nodal tidal cycle in the Kuril Straits that may affect sea surface density in the northwestern North Pacific (where σ_{θ} =26.6 kg m⁻³ outcrops on average), are examined as well. As indicated by constant AOU to nitrate relationships over time, nutrients and other biogeochemical properties are affected similarly to AOU by the physical forcing processes.

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T15: Atmospheric iron inputs and ocean biogeochemical cycles

Mineral dust deposition to the oceans is a key source of dissolved iron to marine ecosystems. However, there are large uncertainties associated with the total mass of dust deposition and with the solubility of the iron within the dust particles. Utilizing the global-scale Biogeochemical Elemental Cycling (BEC) ocean model we examine the sensitivity of marine ecosystem dynamics and associated carbon cycling to spatial and temporal variations in iron inputs from the atmosphere. The BEC model includes multiple potentially growth-limiting nutrients and phytoplankton functional groups, explicit iron cycling, and a newly improved sedimentary source for dissolved iron. We examine the impacts of a spatial-varying iron solubility in mineral dust (relative to the typically assumed low, constant solubility of 1-2%) on phytoplankton community structure and rates of nitrogen fixation, export production, and air-sea CO₂ exchange. We will also investigate the biogeochemical influence of the greatly increased dust deposition to the oceans during the last glacial maximum (LGM). The dust deposition to the Southern Ocean increased by more than a factor of 10 at the LGM. This suggests increased biological export from this iron-limited region, with potentially important downstream effects as subsurface nutrient fields are modified.

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T16: Future ocean biogeochemical cycles' sensitivity and robustness with an Earth system model

In order to address the sensitivity of the potential feedbacks between climate and ocean biogeochemistry we use a global model of the Earth system (LOVECLIM). The standard version of the model predicts that over the next centuries the main change in the biogeochemical oceanic cycle is the significant decrease in silicate content in the euphotic layer at high latitudes. Silicate concentrations in the Southern Ocean drop by as much as 30% in 2300 under scenario A2 when compared to the control run. This model, as most ocean biogeochemical models of application for the study of future global changes, relies on simple parameterizations and on basic biological formulations. This puts serious limitations on any predictive capacity at long time scales. However such models offer the possibility to perform many experiments at a time and so to evidence the most significant processes. In a series of sensitivity studies spanning several centuries we examine the robustness of the predicted changes with respect to different biological parameterizations and formulations.

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T17: Does CO₂ play a role in controlling oceanic N₂ fixation?

Diazotrophic marine cyanobacteria contribute new nitrogen to the world's oligotrophic oceans, but little is known about how they respond to shifts in global change variables such as CO₂. We compared N_2 and CO_2 fixation rates by two important groups of marine N_2 fixers, *Trichodesmium erythraeum* and Crocosphaera sp. during steady-state growth under past, current, and future CO₂ scenarios. At projected year 2100 CO₂ levels (76 Pa, 750 ppm), N₂ fixation rates of both Pacific and Atlantic Trichodesmium isolates increased 35-100%, and CO₂ fixation rates increased 15%-128% relative to present day CO₂ conditions (39 Pa, 380 ppm). CO₂-mediated rate increases were of similar relative magnitude in both P-replete and P-limited cultures, suggesting that this effect may be independent of resource limitation. Neither isolate could grow at 15 Pa (150 ppm) CO₂, but N₂ and CO₂ fixation rates, growth rates, and N:P ratios all increased significantly between 39 and 152 Pa (1500 ppm). Similarly, for Crocosphaera, N₂ and CO₂ fixation increased by 71% and 13%, respectively, under projected 2100 CO₂ levels and decreased by 71% and 67%, respectively, when grown at 190 ppm. These results suggest that by the end of this century, elevated CO₂ could substantially increase global N₂ and CO₂ fixation by two important groups of N₂ fixers and fundamentally alter the current marine N and C cycles, potentially driving some oceanic regimes towards P limitation or limitation by some other element or growth factor. CO₂ limitation of diazotrophy during past glacial periods could also have contributed to setting minimum atmospheric CO₂ levels through down-regulation of the biological pump. The relationship between marine N₂ fixation and atmospheric CO₂ concentration appears to be more complex than previously realized, and needs to be considered in the context of the rapidly changing oligotrophic oceans.

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W20: Incredible Shrinking Iguana: Gaia on Galapagos?

The impact of Galapagos Islands on the cold-tongue has always been conjectured to be important even though high resolution satellite data show a rather local feature to the west of the islands. A forced OGCM coupled to an advective atmospheric model with online-coupled biogeochemistry shows the details of the impacts of Galapagos Islands. The main impact of the islands is to significantly affect the termination of the equatorial undercurrent (EUC), which in turn deepens and diffuses the thermocline. This reduces the mixed layer entrainment and warms the SSTs, which affect the air-sea interactions all the way out to the Dateline. The impact on the ecosystem and biogeochemistry are also significant with warmer SSTs and deeper thermocline leading to more regenerated production whereas the outgassing of the CO₂ from the ocean is reduced due to a weakened solubility pump or reduced ocean pCO₂. This OGCM with biogeochemistry is then coupled to a simple zonal wind anomaly model given by $\tau_x(\lambda, \varphi) = \tau_x \operatorname{clim}(\lambda, \varphi) - \mu(\varphi)(\Delta T - \Delta T_{\operatorname{clim}})$, i.e., the zonal wind-anomaly is proportional to the anomaly of the east-west SST gradient. As can be expected, the impact of Galapagos on the thermocline and the EUC impact the mixed layer-thermocline interactions and hence the Bjerknes feedback and the El Niño-Southern Oscillation (ENSO) cycle itself. The ENSO frequency is reduced to a more realistic quasi-quadrennial period and the amplitude is significantly weakened compared to simulations when the Galapagos Islands are removed from the model configuration. The missing islands result in a far stronger EUC, enhanced entrainment, and completely modify the rechargedischarge cycle on ENSO timescales leading to a much more rapid delayed oscillator. Galapagos thus control not only the annual cycle but also the ENSO frequency and amplitude and in fact render the Galapagos Islands much more habitable for the wide biodiversity for which they have become so well known. The characteristic high-mean, low-variability in the ecosystem and biogeochemistry of the HNLC region itself is determined by the Galapagos!

Yves Plancherel, Andrew Jacobson, Robert Key, and Jorge Sarmiento

T18: Water mass analysis and remineralization stoichiometry using a global non-linear optimization method

A synthetic data set is used to investigate the convergence properties and the accuracy of three algorithms used to solve a set of 9 non-linear water mass mixing equations with unknown stoichiometric coefficients. The analyses demonstrate that the linear scheme (known as optimum multi-parameter) can lead to erroneous results, while the simulated annealing based schemes potentially converge to the true solutions as long as the system is just determined or overdetermined and the parameter space properly sampled.

We implement the simulated annealing scheme to a real oceanic data set for the Indian Ocean and compute the remineralization stoichiometry for each sample and the mixing fractions of the water masses contributing to each sample individually. Concatenated profiles of the remineralization ratios show variability associated with water masses that most likely relate to preformed definition issues. When considering only deep water solutions with low residuals, the C_{org} :N:P ratios of the Indian Ocean seems fairly constant at 106±7:14±1:1, while O₂:P increases with depth from 140 to 180. We propose a deep Si:N of 9 below 4000 m and 5 in the upper 2000 m.

A. Romanou, R. Bleck, G. A. Schmidt, and W. Gregg

T19: Biogeochemical coupling in the NASA-GISS climate model: Preliminary results

A 14-component biogeochemical model (NBOM developed by W. Gregg) is coupled to HYCOM ocean model within the NASA-GISS climate model. The aim is to describe the solubility, biological but also carbonate pumps and the change of their relative roles in a changing climate. Four nutrient, four phytoplankton, 1 zooplankton, 3 detritus components, together with DOC and DIC comprise the biogeochemical space the model solves in. Spectral irradiances are transferred to the ocean and are altered by the ocean biology at surface and in depth. The ensuing upwelling radiance changes the albedo and the energy budget at the surface of the ocean.

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T20: Update on the Fourth Primary Productivity Algorithm Round Robin (PPARR4)

Modeling oceanic primary production (PP) on the basis of satellite measurements of ocean color has great potential for biogeochemical studies, especially in order to better understand the carbon cycle at a global scale. In fact, direct PP measurements are not only expensive and time-consuming, but are affected by significant variability in space and time as well as by sampling errors. Therefore, calibration and validation of PP models are not straightforward and differences between model estimates may be quite large. The Primary Production Algorithm Round Robin (PPARR) studies aim to explore model variability through a series of comparison exercises. Our prior research compared various models that estimate depth-integrated PP using remote satellite data, as well as those that use general circulation models coupled with ecosystem or biogeochemical models. We found that greater variability between modeled estimates of PP occurred at low sea surface temperature (SST) and low or high chlorophyll concentrations. This suggests that current PP models lack accuracy in cooler waters such as the Southern Ocean (SST < 10° C), eutrophic waters such as coastal zones, oligotrophic sub-tropical gyres, and in high-nutrient low-chlorophyll areas such as the equatorial Pacific.

We have now expanded the PPARR project into its fourth exercise by comparing participating PP models with in situ PP data acquired during JGOFS process studies and time-series sites [i.e. Bermuda Atlantic Times-Series Study (BATS)], data from the Southern Ocean and equatorial Pacific, and a compilation of coastal measurements. Results from the equatorial Pacific comparison revealed that the PP models consistently underestimated the variance of depth-integrated PP. The simplest models (depth- and wavelength-integrated) performed as well as some of the most complex models (depth- and wavelength-resolved). A testimony of the success of the PPARR project is the significant decrease in root-mean-square error of participating models in the equatorial Pacific (by 62% on the equator and 35% off the equator) between earlier PPARR exercises and more recent ones. Here, we present preliminary results comparing in situ PP data from BATS to modeled PP using both in situ and remotely sensed chlorophyll data. This enables us to distinguish between errors in PP estimates resulting from remotely sensed chlorophyll, and errors due to inherent PP model limitations.

We encourage further model participation in the PPARR4 project. Researchers with potential PP models who would like to participate can contact either V. Saba (vssaba@vims.edu), M.-E. Carr (carr@jpl.nasa.gov), or M. Friedrichs (marjy@vims.edu).

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W2: Coastal observing at CRIMP-CO₂, Kaneohe Bay, Hawaii: A study of land-ocean interactions and CO₂ exchange between seawater and the atmosphere

Human activities throughout the past two centuries have broadly changed the landscape of our environment. Changes in land use and fossil fuel burning associated with global industrialization have led to large increases in the atmospheric content of greenhouse gases and are now widely thought to cause global warming. It is also thought that climate change may increase the frequency of storms. The latter facilitate the transfer of nutrients, sediment, and pollutants from rivers into coastal ecosystems, potentially contributing to changes in how the coastal area responds to natural forcing mechanisms. There is mounting evidence that increased oceanic CO_2 concentrations lower the saturation state of seawater with respect to carbonate minerals, cause "ocean acidification" and, it has been argued by some, negatively impact calcification (e.g., Kleypas et al., 1999; Orr et al., 2005). Coastal areas and estuaries, however, may be either net annual sources or sinks of atmospheric CO_2 (-41 to 7.3 Mole C m⁻² yr⁻¹, Mackenzie and Lerman, 2006), depending on local conditions.

We present here results from 18 months of observations at CRIMP-CO₂, a collaborative effort in Kaneohe Bay, Hawaii between UH Manoa and NOAA/PMEL. This buoy was the first coastal buoy of the NOAA/PMEL-CO₂ program. CRIMP-CO₂ has documented the response of bay waters to pulsed inputs throughout a La Niña winter season (2005-06) and a much drier subsequent winter (2006-07). The evolution of bay waters following storm-derived inputs of freshwater, sediment, and nutrients was studied, along with the impacts of blooms and physical forcing on the air-sea exchange of CO₂. Although nutrient inputs typically cause phytoplankton blooms in Kaneohe Bay, physical forcing strongly influences system response, in particular stratification and mixing, hence controls both the duration of blooms and attendant changes in CO₂ concentration. Southern Kaneohe Bay offen becomes a CO₂ sink following storm inputs (0.2-0.7 m Mole C m⁻² hr⁻¹), but remained a net source of CO₂ to the atmosphere (-1.06 Mole C m⁻² yr⁻¹) throughout our study period. This result is similar to estimates from Hog Reef flat in Bermuda and from the Scheldt Estuary plume (-1.2 and -1.1 to -1.9 Mole C m⁻² yr⁻¹, respectively, Mackenzie and Lerman, 2006).

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W3: Rising CO₂ conditions and ocean acidification - a severe threat to high latitude coastal ecosystems

Since the onset of industrialization various activities of mankind have increased the atmospheric CO_2 partial pressure (pCO₂) from approximately 280 ppm to 380 ppm nowadays. Part of this anthropogenic CO_2 is taken up by the oceans causing an increase of the oceanic pool of dissolved inorganic carbon (DIC), which in turn causes a readjustment of the CO₂-system equilibrium: the dissolved CO_2

concentration increases, while the pH and the carbonate ion concentration (CO_3^{2-}) decrease. Hitherto, little attention has been devoted to the effects of rising CO₂ conditions on the CO₂ and ecosystems of (higher latitude) coastal oceans. The North Sea, a northwestern European shelf sea, constitutes an ideal site for investigations of these effects and their consequences, since during the recent years comprehensive insight has been gained into the North Sea's carbon cycle.

New observations from the North Sea show that between 2001 and 2005 the CO₂ partial pressure (pCO_2) in surface waters rose faster than atmospheric pCO_2 . The decline in air-sea partial pressure difference (ΔpCO_2) reflects partly a theoretically predicted feedback loop also evident in data and models for the entire North Atlantic: the invasion of anthropogenic CO₂ reduces the ocean's CO₂ buffer capacity and its ability to uptake additional CO₂. The hydrochemical and water column conditions cause this effect to be more accentuated in the North Sea as a consequence of advective and in situ processes.

The accelerating decrease of the buffer capacity reflects a decrease of the $CO_3^{2^-}$ concentration and in turn a decrease of the saturation states of Calcite and Aragonite. The reported dependence of the calcification activity on the saturation state implies a severe decline in calcification in the North Sea between 2001 and 2005. Rising CO_2 conditions thus exert high pressure on high latitude coastal ecosystems, which last but not least play a crucial role in the world's food supply.

Vinu Valsala

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W4: Design and validation of an offline oceanic tracer transport model for carbon cycle study

An offline passive tracer transport model with self-operating diagnostic mode vertical mixing and horizontal diffusion parameterizations is used with assimilated ocean currents to find the CFC-11 cycle in oceans. This model is developed in NIES under carbon cycle research project inside the GOSAT (Greenhouse gas Observing SATellite) modeling group. The model borrows offline fields from precalculated monthly archives of assimilated ocean currents, temperature and salinity, and evolves a prognostic passive tracer with prescribed surface forcing. The model's performance is validated by simulating CFC-11 cycle in the ocean starting from the pre-industrial period (1938) with observed anthropogenic perturbations of atmospheric CFC-11 to comply with OCMIP-II flux protocol. The model results are compared with ship observations as well as the results of candidate models of OCMIP-II and a performance is assessed. The model simulates the deep ventilation processes in the Atlantic Ocean appreciably well and yields a good agreement in column inventory of CFC-11 amplitude and phase compared to the observation. The statistical skill test shows that this model outperforms other candidate models of OCMIP-II because of its higher resolution and assimilated offline inputs feeding and shows a potential role in improving transport calculation in the ocean with cost-effective computation.

Marian Westley

NOAA Geophysical Fluid Dynamics Laboratory, Princeton, NJ

W5: Predicting changes in the oceanic nitrous oxide cycle with changes in the volume and extent of suboxia

The low oxygen regions of the world's oceans are known as sites of subsurface accumulation of nitrous oxide, an atmospheric trace gas that contributes to greenhouse warming in the troposphere and ozone destruction in the stratosphere. Nitrous oxide can be produced in the ocean as an intermediate of heterotrophic denitrification, the respiration of organic matter using nitrogen oxides as electron acceptors in lieu of oxygen, and as a byproduct of nitrification, the stepwise oxidation of ammonia to nitrite and nitrate. The yield of nitrous oxide from both pathways is enhanced by low oxygen conditions. Measurements of the concentration and isotopomer distribution of nitrous oxide in the eastern tropical North Pacific support the hypothesis that the subsurface nitrous oxide maximum in this region results from nitrifier denitrification, and furthermore, that nitrous oxide is both produced and consumed within the subsurface concentration maximum. Bottle incubation experiments with ¹⁵N-labelled ammonia and nitrite confirm the predominance of a reductive pathway to nitrous oxide while also demonstrating active conversion of ammonia to the dissolved nitrate/nitrite pool. We present a simple one-dimensional model to describe the redox cycling of nitrogen under suboxic conditions and to forecast the response of the ocean's nitrous oxide source to changes in the volume and extent of oceanic suboxia.

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W6: Time-series of fCO2 at Station P (50°N, 145°W) and Line P in sub-arctic NE Pacific

The DFO Climate Chemistry Laboratory has been carrying out time-series observations of pCO_2 (partial pressure of CO_2) in the surface waters at Station P (50°N, 145°W) in the sub-arctic NE Pacific Ocean and in Line P between Station P and the mouth of Juan de Fuca Strait just south of Vancouver Island. Time-series of SST (sea surface temperature), salinity, DIC (dissolved inorganic carbon) and alkalinity at Station P are shown. Time-series of fCO₂ (fugacity of CO₂), average DIC in the surface mixed layer, detrended DIC and nDIC, (normalized to salinity 32.6 psu as 10-years mean), and seasonal detrended fCO₂ are also displayed. The change in fCO₂ by biological effect, temperature change and air-sea gas exchange are evaluated. The seasonal change of DIC, Chl-a (chlorophyll-a), fCO₂, DIC and alkalinity along Line P are shown. FCO₂ and DIC have been increasing by 24.33 µatm and 7.82 µmol kg⁻¹ between 1994 and 2003, or 2.43 µatm per year and 0.78 µmol kg⁻¹ per year, respectively.

THEME 3. TERRESTRIAL/COASTAL OCEAN CROSS-BOUNDARY FLUXES

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W7: Contrasting dynamics of high molecular weight dissolved organic carbon in the Chesapeake Bay and coastal ocean: Insights from enzyme activities, carbohydrate inventories, and microbial metabolism

The interactions between heterotrophic microbial communities and high molecular weight dissolved organic carbon (DOC) in riverine and marine environments are highly complex. The molecular-scale composition of DOC has been painstakingly documented in a number of studies (e.g. Mannino and Harvey 2000; Minor et al. 2006), revealing that high molecular weight (HMW) carbohydrates, specifically polysaccharides, constitute a significant fraction of estuarine as well as marine DOC. Within classes of HMW DOC, however, dynamic and compositional information remains elusive. Furthermore, low molecular weight (LMW) DOC, which is typically 60%-80% of all DOC, has been much more resistant to characterization, because many methods used to characterize DOC begin with a concentration step in which LMW DOC is lost (e.g., Benner 2002). Thus, interactions between the pools of HMW DOC and LMW DOC, in particular the production of LMW DOC from HMW DOC by extracellular enzymes and its subsequent uptake by heterotrophic microbes, have been difficult to characterize. The objective of this study therefore was to examine the enzymatic potential and substrate preferences of microbial communities along a riverine-marine transect, the ability of these communities to process dissolved carbohydrates, and linkages between different steps in degradation of the COC pool.

Rates of enzymatic hydrolysis of a suite of polysaccharides were measured concurrently with total carbohydrate and monosaccharide concentrations, bacterioplankton abundance, and glucose assimilation rate constants. These measurements revealed that one third to one half of the monosaccharide pool could have been produced daily by enzymatic hydrolysis of polysaccharides. In the river and bay, daily enzymatic production of monosaccharides was 16-68% of total carbohydrates. implying turnover of those pools on a time scale of hours to days. At a marine site, in contrast, apparent turnover of the monosaccharide pool was considerably slower (4-8% day⁻¹), implying turnover times of weeks or more. In the river and bay, rapid hydrolysis of polysaccharides relative to carbohydrate inventories suggests that there is substantial flow of organic carbon from autochthonous or allochthonous sources into the pool of dissolved polysaccharides, and this pool is on the whole highly reactive. However, very low hydrolysis rates of two specific polysaccharides at all sites suggest that some polysaccharides may be essentially unavailable to the microbial communities at times. despite the fact that these same polysaccharides are readily hydrolyzed in other marine locations (Arnosti et al., 2005). Carbohydrate cycling in the river and bay was very dynamic, far surpassing rates at the marine site. Nonetheless, specific components of the polysaccharide pool in the river and bay may be exported intact from the estuary into the ocean. Given slower rates of cycling at the marine site, these polysaccharides likely fuel heterotrophic metabolism at locations quite distant from their sources.

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W8: Natural isotopic (¹⁴C and ¹³C) and stoichiometric approaches for assessing the sources and fates of organic matter in ocean margins: Findings from the Middle and South Atlantic Bights

Organic matter in continental shelf and slope waters may originate from a variety of potential sources. This results, at least in part, from ocean margins comprising the interface between land and the open ocean, as well as the greater relative effects of seafloor and atmospheric exchanges on limited-volume shelf waters. Greater variability in the concentrations, as well as both the chemical and isotopic

compositions of dissolved and particulate organic matter (DOM and POM, respectively) in margins compared to the open ocean is consistent with a greater diversity of organic matter sources in these systems. One possible outcome of the unique forms and combinations of autochthonous and allochthonous organic matter in ocean margins is differences in system metabolism between individual margins, as well as between margins and systems dominated by marine organic matter exclusively (e.g., pelagic ocean). Recent findings from the Middle and South Atlantic Bights (MAB and SAB, respectively) indicate that the DOM and POM in both margins have fundamentally different sourceage signatures. That is, DOM is derived predominantly from an admixture of aged marine and modern terrestrial materials; in contrast, POM is derived from highly aged terrestrial and young marine materials. Compared to the MAB, the SAB contains greater amounts of DOC that is simultaneously ¹³C-depleted and ¹⁴C-enriched, suggesting larger inputs of young, terrestrial material there, especially on the inner- and mid-shelf. Dual isotope and multi-property mass balances are further used to constrain the contributions of allochthonous and autochthonous organic matter to the waters of both systems.

Terrestrial sources, whether of young DOM or aged POM, were always N- (and generally P-) depleted relative to their marine counterparts, leading to net terrestrial organic C inputs that could help support excess respiration in certain margins. DOC degradation rates were about 2-fold lower in the SAB than the MAB, but stoichiometric (C:N) increases in degraded DOM were greater in the SAB and grew progressively larger from the inner to outer shelf. Significant shifts in the Δ^{14} C signatures of DOC during degradation revealed that a bomb ¹⁴C-enriched component was preferentially remineralized to CO₂, leaving a highly ¹⁴C- and N-depleted refractory fraction for offshore export from the SAB to the interior North Atlantic. Additional studies of microbial and photochemical degradation of DOM from rivers and estuaries in the MAB-SAB region further demonstrate significant alterations in the terrestrial signal that imparts a more "marine-like" character to the degraded material, potentially confounding the terrestrial input term to margins and the oceans in general.

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W9: Carbonate dissolution in shallow water carbonate platform sediments

We have estimated carbonate dissolution rates for sediments on the Bahamas Bank using an inverse pore water advection/diffusion/reaction model applied to pore water O_2 , alkalinity, and DIC profiles. The sites we have studied include ooid sands, grapestone deposits, and aragonite muds, with a wide range of seagrass densities. Integrated rates of carbonate dissolution at these sites (i.e., dissolution fluxes) range from <2 mmol m⁻² d⁻¹ (ooid sands with no seagrass coverage) to ~80 mmol m⁻² d⁻¹ for sediments underlying dense seagrass beds. These carbonate dissolution fluxes are also positively correlated with seagrass density. In part this occurs because sub-surface pumping of photosynthetically produced O_2 from seagrass roots and rhizomes is a major driver of benthic aerobic respiration (and hence metabolic carbonate dissolution) in these sediments.

Our studies further indicate that high-Mg calcite (HMC; ~12 mole% Mg) undergoes preferential dissolution in these sediments. At the same time, the dissolution we observe is actually net dissolution (i.e., the balance between gross dissolution and re-precipitation). The secondary phase that forms has a Mg content that is only a slightly lower than that of the starting material. These results therefore

suggest that HMC dissolution/re-precipitation occurs in Bahamas Bank sediments as a result of "Ostwald ripening," in which smaller carbonate grains dissolve at the expense of secondary carbonates that form on the surface of larger grains.

Using our results, dissolution fluxes integrated over the entire Bahamas Bank are $\sim 3 \text{ mol m}^{-2} \text{ yr}^{-1}$, and are of similar magnitude to gross carbonate production fluxes ($\sim 5 \text{ mol m}^{-2} \text{ yr}^{-1}$). When the carbonate dissolution rates estimated here are examined in the context of carbonate budgets for shallow water carbonate platforms, they suggest that carbonate dissolution may be a significant loss term in these budgets. Furthermore, depending on the magnitude of offshore transport of platform carbonates, these results also raise important questions about the steady-state nature of these carbonate budgets.

The occurrence of coupled dissolution/re-precipitation may impact the way in which shallow water HMC acts as a buffer for rising atmospheric CO_2 , depending on whether the solubility and/or kinetic reactivity of the secondary phase differs significantly from that of the initial phase. Given the dynamics of these processes, the seagrass-mediated carbonate dissolution we have observed may also exert a negative feedback on rising atmospheric CO_2 , although the magnitude of this effect remains to be quantified.

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W10: Air-sea CO₂ flux and control mechanisms in the US east coast and other western boundary current shelves

It is increasingly recognized that air-sea CO_2 flux and carbon budget in continental margins represent an important knowledge gap in global carbon cycling research. On the east coast of North America, until very recently, the US Mid-Atlantic Bight is the only shelf that annual air-sea CO₂ flux was measured. While this shelf acts as a moderate-to-strong sink of atmospheric CO₂, its overall carbon flux to the open ocean is not known. The central part of the South Atlantic Bight (SAB) was reported as a source of CO₂ to the atmosphere as a result of decomposition of organic matter exported from rivers and the productive salt marshes. Our recent whole shelf seasonal survey, however, defines the entire SAB as a weak CO₂ sink while the inner shelf remains as a CO₂ source. Large seasonal changes occur mostly in the spring and fall. It appears that temperature is the most important control on surface pCO₂ and that organic carbon production and respiration are well coupled in the SAB. Preliminary data collected in the Gulf of Mexico (GOM) suggest that air-sea CO₂ flux and carbon recycling are extremely patchy with the freshwater dominated area being a strong CO₂ sink and the rest of GOM most likely a CO₂ source. Because of its large area and strong signal, the size and direction of the CO₂ flux in the GOM would have a major influence on the overall coastal ocean air-sea CO₂ budget in the North America. In the northern end of the North America east coast, the Gulf of Maine and the Nova Scotia shelf is most likely a moderate sink of atmospheric CO₂ although reliable data are limited to its southern-end (Vandemark and Salisbury, pers. comm.). Characteristics of these and a few other western boundary current shelves are compared. Temperature, terrestrial input, shelf depth and stratification, existence of spring bloom, etc. are identified as the most important factors controlling the carbon cycling and the size and direction of air-sea CO₂ flux.

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W11: Interannual variability of nutrient fluxes in the Slope Sea due to shelf water entrainment by Gulf Stream warm-core rings in response to the North Atlantic Oscillation

The common occurrence of Gulf Stream warm-core rings (WCRs) in the Slope Sea (SS) and their role in initiating cross-frontal events like shelf water entrainment in the western North Atlantic (WNA) have been well documented. Moreover, WCRs have also been shown to significantly affect the physical, chemical and biological oceanography of the SS region. However, most reported results concerning WCRs have been deduced from single surveys or time-series surveys from individual WCRs. Long term impacts of these energetic features and their inter-annual variability (IAV) have not been studied. This work will investigate the impact of shelf water entrainment by WCRs into the WNA SS between 75° and 50°W over a 22 year period from 1978 to 1999. Preliminary results suggest a significant response of WCR activity to climate variability related to the state of the North Atlantic Oscillation (NAO) such that positive (negative) NAO years correspond to more (less) occurrences of WCRs. We hypothesize that higher numbers of WCRs generated during positive NAO years would increase the probability of entrainment events and result in higher fluxes of shelf water being advected into the SS. A two-dimensional Quasi-Geostrophic Potential Vorticity (QGPV) model is used to determine annual estimates of shelf water volume fluxes into the SS by WCRs. The entrainment of nutrient rich waters from the outer continental shelf by WCRs to the SS significantly influences the nutrient budgets of both the shelf and slope regions. Changes in the shelf water volume flux estimates are used to study the IAV of offshore advection of macro-nutrients from the continental shelf caused by WCR entrainment. Fluxes of nitrate (NO)₃ and silicate (Si(OH)₄) transported by shelf waters entrained into the SS by WCRs vary interannually with higher advective (lower) fluxes in years when the NAO is positive (negative) augmented by increased (decreased) WCR activity.

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W12: Importance of lateral transport in margin-to-deep-ocean export of organic carbon: A regional (Northwest Atlantic) and global perspective.

Water column and sedimentary processes on continental margins are complex, spatially heterogeneous and dynamic. They tend to be highly productive systems with significant carbon burial on the margins. Organic carbon supplied to and produced over the margins can also be exported to the deep ocean via a range of processes. The importance of lateral carbon transport in terms of its impact on deep ocean biogeochemistry and carbon burial, however, remains uncertain.

The Northwest Atlantic margin is characterized by the existence of strong and persistent, intermediate depth nepheloid layers emanating from the continental shelves, and bottom nepheloid layers maintained by strong bottom currents associated with the southward flowing Deep Western Boundary Current (DWBC) and its interactions with the northeasterly flowing Gulf Stream. These features provide conduits for export of organic carbon to the interior ocean. As part of a project to understand

dynamics of particulate organic carbon (POC) on the NW Atlantic margin, we collected suspended and sinking POC using with in-situ filtration devices and time-series sediment traps, respectively, deployed over the New England Slope. Sampling sites were closely aligned with the "Line W" physical oceanographic mooring array that provides hydrographic context for the samples collected and also an assessment of the dynamics of the particle field in the vicinity of the DWBC. Isotopic and molecularlevel characteristics of the organic matter were used to assess inputs and modes of supply of POC.

Geochemical and flux measurements provide strong evidence for significant lateral transport of organic matter over the NW Atlantic margin. These include (*i*) frequent occurrences of higher fluxes in deep relative to shallow sediment traps, with different periods of increased fluxes intercepted by these traps; (*ii*) low Δ^{14} C values and alkenone-derived temperatures of suspended and sinking POC, indicating supply of pre-aged carbon formed in cooler surface waters; (*iii*) a strong correlation between Δ^{14} C values and aluminum concentrations, implying supply of lithogenic (shelf-derived) particles to depth.

A broader survey of available radiocarbon and aluminum data for sinking particles recovered from other ocean regions suggests that lateral supply of pre-aged, shelf-derived POC to the deep ocean is a widespread phenomenon and warrants further investigation in terms of the importance of advective processes as a mode of removal of carbon from surface reservoirs.

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W21: Eurasian warming-driven changes in the hydrography and biological productivity of the Arabian Sea

The mid-latitudinal continental warming trend in the Northern Hemisphere and the progressive decline in winter and spring snow cover over the Eurasian continent, in particular over southwest Asia and the Himalayan/Tibetan region since the mid-90's, is causing a land-ocean thermal gradient that is particularly favorable to stronger southwest (summer) monsoonal sea surface winds. Since 1997, sea surface winds have been strengthening in the western Arabian Sea. This escalation in the intensity of winds has brought about an intensification of coastal upwelling, leading to a profound increase in average summer time chlorophyll a concentrations off the coast of Somalia. Offshore over a wider region in the western Arabian Sea also, chlorophyll concentrations have been on the rise due to increased advection of newly upwelled, nutrient-rich water away from the coast into the central Arabian Sea by wind-generated coastal filaments and jets. The extraordinarily large increase in chlorophyll in the western Arabian Sea has raised the intriguing possibility that the current warming trend of the Eurasian landmass is making the Arabian Sea more productive. We also provide evidence that warming trend is undermining cooling responsible for convective mixing during the northeast monsoon. The consequences of the climatic warming trend and changes in phytoplankton productivity on carbon cycling, biogeochemical processes and fisheries in the Arabian Sea, will be discussed in light of these findings.

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W13: Examining distributions and controlling mechanisms of pCO_2 and air-sea fluxes of CO_2 in the northern Gulf of Mexico

Carbon dioxide (CO₂) is the major currency during biological production or destruction of organic matter (OM) and is the dominant greenhouse gas. Atmospheric CO₂ is fixed into biomass in the land and is subsequently transported via rivers into the ocean where it may be metabolized back to inorganic carbon and either released back to the atmosphere or exported into the deep ocean. Thus CO_2 flux between the atmosphere and the ocean is a critical variable in global carbon cycle models. An argument can be made that increasing terrestrial inputs associated with land use change, increasing discharge of sewage and other anthropogenic materials, and changes in the terrestrial hydrological cycle would tend to shift the coastal oceans in particular toward being a source of CO_2 . Margin ecosystems receive massive inputs of terrestrial organic and mineral matter and exhibit intense geochemical and biological processing of carbon and other elements. In addition, they exchange large amounts of matter and energy with the open ocean. The complex and variable nature of coastal margins poses significant challenges to efforts to characterize the carbon signals in these regions. We have employed a combined strategy of ship-based and satellite observations to provide spatial and temporal coverage for broad scale assessments of pCO_2 distributions and air-sea fluxes of CO₂. The primary objective of our research is to apply these approaches to the characterization of pCO_2 and airsea fluxes of CO_2 in the river influenced margin of the northern Gulf of Mexico.

Our recent findings in the vicinity of the Mississippi River plume demonstrate the potential for this system to act as both sink and source of carbon dioxide. The results also reveal the highly variable nature of carbon fluxes in this system, and the need for both greater spatial and temporal coverage as well as an assessment of the underlying community metabolism driving patterns in surface CO₂. Airsea fluxes of CO₂ for the region around the Mississippi delta range from a net uptake of -4 mmol C m⁻² d⁻¹ in June 2003 to a net release of 96 mmol C m⁻² d⁻¹ in October 2005. Our findings suggest the late spring and early summer is a period of lower surface pCO_2 corresponding to a strong biological pump and autotrophic fixation of inorganic carbon. Other key environmental drivers appear to be seasonal variations in temperature and freshwater discharge. Algorithms relating surface pCO_2 to environmental variables, for example, as can be retrieved from satellite imagery, will necessarily have to account for such changes in system properties. This effort will benefit from more extensive in situ data, including ship-based surveys and moored time-series.

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W14: Dissolved Organic Carbon in the Cariaco Basin

Measurements of dissolved organic carbon (DOC), dissolved inorganic carbon (DIC) and dissolved organic nitrogen (DON) were made at the CARIACO time-series station (10°30' N, 64°40' W), in the southeastern Caribbean Sea, as part of the CARIACO time-series program. There was a marked seasonal variability in DOC concentrations, with lower values (\sim 70 μ MC) during the upwelling season

(December-May), due to the injection of cold, DOC-depleted Subtropical Underwater (SUW) near the coast. During the rainy season (June-November) waters were highly stratified and DOC accumulated in the upper 100m of the water column, increasing to ~90 μ MC. DOC concentrations decreased with depth, from a yearly average of ~80 μ MC at the surface to ~55 μ MC at 1310m. DOC and DIC correlated well throughout the water column: DOC decreased with increasing depth, while DIC increased in concentration. A DOC increase of ~1-10 μ MC was repeatedly observed at the oxic/anoxic interface, currently attributed to bacterial production. A similar increase was also observed in DON concentrations at the same depth. There was no apparent relationship between DON and DOC throughout the water column, indicating that N and C have different residence times and removal processes within the Cariaco Basin. DOC/DON ratios did not vary significantly with season or depth (~13.2 ± 0.91 mol C mol N⁻¹), agreeing well with ratios observed in other upwelling areas. Most local rivers do not contribute significant DOC concentrations to the Cariaco Basin. However, the Tuy River is a source of dissolved organic carbon to the Western Basin, both during the upwelling and rainy season. The contribution from the Tuy River does not reach the CARIACO Time-Series station.

B. Greg Mitchell, Sarah T. Gille, Christopher D. Hewes, Mati Kahru, Osmund Holm-Hansen, Rick A. Reynolds, and Haili Wang

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M13: Shelf-derived iron transport mechanisms regulate the Drake Passage plankton ecosystem transition

The Shackleton Transverse Ridge (STR) in Drake Passage defines a boundary between low and high phytoplankton waters. Satellite, ship and drifter data indicate that the Southern Antarctic Circumpolar Current Front (SACCF) is steered south by the STR toward the Antarctic Peninsula shelf near Elephant Island and then returns offshore carrying elevated iron. This natural mechanism for crossboundary flux of shelf-derived iron from the continental shelf to the pelagic ocean has significant effects on the observed phytoplankton pattern including elevated values of chlorophyll, primary production and export production for iron-enriched waters. Phytoplankton photosynthesis parameters (PvsE and Fv/Fm) indicated relatively more Fe stress in ACC waters (low Fe) compared to mixed waters or shelf breakwaters east of the STR. In the SACCF jet defined by surface drifters and satellite altimetry, cyclonic eddies retain phytoplankton within the eddy cores, limit vertical mixing by lifting the isopycnal surfaces and contribute to cross-front exchange of denser Weddell Sea water that provides a lower boundary for mixing. Anticyclonic eddies have low Chl-a in the core but increased Chl-a in the periphery. Cross boundary mixing between ACC and Weddell Seat water mediated by eddies transports nutrients (e.g. Fe and Si) to the north and contributes to the increased Chl-a in the frontal zone. Interannual variations in the cyclonic eddy activity are positively correlated with variations in Chl-a during the spring bloom in regions of the Antarctic Circumpolar Current around South Georgia. These important physical dynamics regulate iron delivery and hence ocean biogeochemistry across the Drake Passage plankton ecosystem transition. Climate change may accelerate glacial melt water delivery to the region further enhancing iron fluxes from the terrestrial system to shelf waters.

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W16: 2007 moored observations at Station HL2 on the Scotian Shelf

The decline of a spring bloom on the Scotian Shelf is examined using an array of autonomous instruments deployed at a mooring site. A SeaHorse profiler and a CARIOCA buoy provide physical, biological and chemical measurements with very high temporal resolution. The profiler makes highly vertically resolved measurements of water temperature, salinity, fluorescence while the CARIOCA buoy makes hourly measurements of surface water pCO₂, near-surface water temperature, salinity, pressure, air temperature and wind speed, as well as fluorescence. The measurements are complimented by frequent shipboard sampling at the mooring station (HL2) as part of the Atlantic Zone Monitoring Program (AZMP). Measurements obtained at HL2 from early April to early July of 2007 are presented.

Surface water pCO_2 increases from a minimum of 220 ppm during the bloom period and is highly correlated with the rise in near-surface water temperature. The temperature control on pCO_2 is examined by normalizing all pCO_2 values to a constant temperature. Measurements of pCO_2 from the buoy are found to be in good agreement with shipboard measurements taken at station HL2 using an underway pCO_2 system. Observations of chlorophyll concentration are corrected for daytime photochemical quenching; the expected inverse relationship between chlorophyll concentration and surface water pCO_2 is observed throughout the measurement period.

Porchè Spence, Deanna Osmond, Wayne Robarge, and Wesley Childres

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W17: Passive overland runoff sampling system design for residential lawns

Nitrogen export associated with overland runoff from residential landscapes as a function of lawn treatment differences remains poorly defined. The objective is to design a passive runoff sampling system to quantify the amount of N lost through surface runoff from residential lawns under different management practices. The different management practices include a high maintenance fescue lawn, a low maintenance fescue lawn, and a forested residential landscape with periwinkle under story and leaf litter. Artificial catchments, approximately 400 ft² in area, have been delineated in each lawn by installing metal landscape edging 2 inches deep into the soil. The catchments are shaped to direct the overland runoff flow through the 10-runoff outlet ports, which are spaced 3 inches apart and $1\frac{1}{2}$ inches from the top of the edging. Runoff will be collected in 20-L sterile Nalgene media bags, which are manufactured to protect against UV light, carbon dioxide, oxygen, and water vapor. The rational and orifice equations have been used to estimate the peak flow rate the system is capable of withstanding during a 24-hour 25-year rain event. The storm peak flow approximations have ensured that the water collected from passive sampler design would not surpass the system's collection ability. One 20-L media collection bag connected to ¹/₂ inch PVC tubing is attached to the randomly chosen 4th, 6th, and 9th outlet ports to collect 100% of the surface runoff volume. A 1/2 inch squared screen in front of a finer mesh screen held by landscape staples in front of the outlet ports minimizes the quantity of leaf litter and large soil particles flowing through system and into the collection bags. Using the catchment's surface area and 57-year Raleigh daily record precipitation averages, the runoff volumes and flow rate have been used to calculate the expected runoff volume generated within each lawn during extreme storm events. The passive sampling system is an effective and efficient apparatus in collecting the overland flow samples.

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W18: The observed impact of rivers on CO₂ dynamics in the coastal Gulf of Maine

The Gulf of Maine is a productive mid-latitude ecosystem displaying both open ocean and coastal characteristics. Freshwater flux to the Western Gulf from New England watersheds is substantial relative to most eastern U.S. freshwater inputs and the role that this flux plays in affecting the carbon cycle remains an open question. A monthly observational program spanning 2004-present provides new cruise data collected in part to address land-ocean interaction issues and has recently been augmented by a continuous pCO_2 buoy measurement system offshore of NH. Surface layer pCO_2 and dissolved oxygen measurements are being collected alongside ancillary biological, physical, and chemical data from flow-through, discrete sample, and profiling systems. We have observed seasonal and episodic signatures with high covariance between riverine input, biological productivity, and the metabolic surrogates pCO_2 and DO. Unusually high levels of freshwater drove Western Gulf of Maine salinity levels downward in 2005 and 2006. This work will address perturbations of this coastal ecosystem's carbon budget and air-sea pCO_2 fluxes associated with these events.

SPECIAL POSTER PRESENTATION (Clark 5, MTW – Easel):

Cyndy Chandler¹, David Glover¹, Robert Groman², Peter Wiebe²

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An Introduction to the Biological and Chemical Oceanography Data Management Office (BCO-DMO)

The BCO-DMO (http://www.bco-dmo.org) was created to serve PIs funded by the NSF Biological and Chemical Oceanography Sections as a facility where marine biogeochemical and ecological data and information developed in the course of scientific research can easily be disseminated, protected, and stored on short and intermediate time frames. The Data Management Office also strives to provide research scientists and others with the tools and systems necessary to work with marine biogeochemical and ecological data from heterogeneous sources with increased efficacy. To accomplish this, two data management offices (former- U.S. JGOFS and U.S. GLOBEC) have been united and enhanced to provide a venue for contribution of electronic data/metadata and other information for open distribution via the World Wide Web.

The JGOFS/GLOBEC Client/Server distributed data management system software is used to serve data and information to every investigator, regardless of computing platform. In addition, Web services are provided for data discovery, and development has begun on a machine-to-machine application programming interface (API) to allow interoperability between Web-based data systems. The BCO-DMO will manage existing and new data sets from individual scientific investigators, collaborative groups of investigators, and data management offices of larger multi-institutional projects via any standard Web browser. The office will work with principal investigators on data quality control; maintain an inventory and program thesaurus of strictly defined field names; generate metadata (e.g. Directory Interchange Format (DIF)) records required by Federal agencies; ensure submission of data to national data centers; support and encourage data synthesis by providing new,

online, Web-based display tools; facilitate interoperability among different data portals; and facilitate regional, national, and international data and information exchange.