Ocean Carbon and Biogeochemistry (OCB) Summer Workshop
Woods Hole Oceanographic Institution, Clark 507
July 21-24, 2014

POSTER ABSTRACTS

The Coupled North Atlantic-Arctic System: Processes and Dynamics (Monday, 7/21)

Anticyclones enhance *Prochlorococcus* and particle export in the Sargasso Sea

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We examined the biogeochemical properties in the Sargasso Sea during four cruises in 2011-2012 (two in spring, two in summer) and our objective was to determine how variability in these measurements may be explained by mesoscale phenomena. Do ecosystems that develop in mesoscale eddies differ from ecosystems at the Bermuda Atlantic Time-series Study (BATS) site, that was not directly impacted by eddies (in most cases)? We sampled four eddies (two anticyclones, two cyclones) and characterized the nutrient environment and microbial (phytoplankton and heterotrophic bacteria) stocks, primary production (PP) and measured particle (POC) export to determine how eddies altered the ecosystem function compared to seasonally-mediated conditions at BATS. While all eddies we investigated perturbed the seasonally-mediated water column structure and impacted the microbial community, especially intriguing were the two anticyclones that enhanced POC export. In spring 2011 biomass and PP in the center of anticyclone AC1 (age 6 months) was lower than BATS and the picophytoplankton community was dominated by *Prochlorococcus* (*Pro*) but thorium-234 POC export was 56-72% greater via downwelling at the center of AC1. Eddy-wind interactions in summer 2012 caused upwelling at the center of anticyclone AC2 (age 1 month). Phytoplankton biomass, *Pro* populations, and PP rates were greater in AC2, specifically at the edge (which interacted with a cyclone) and coincided with high thorium-234 POC export. While biomass was greater in the two cyclones (compared to BATS), the impact of these eddies on POC export appeared to be more short-term and seasonally dependent than the anticyclones. These data demonstrate that the role warm-core (non-mode water) eddies play in carbon cycling may have been previously underestimated in the Sargasso Sea.

Inter-annual variability of the shelf break front position between 75° and 50° W

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The shelf break front located off the eastern seaboard of the U.S. and Canada is a continuous front running from Cape Hatteras, North Carolina, to the Tail of the Grand Banks, south of Newfoundland and separates colder and less-saline shelf waters from warmer and more saline slope waters. The front is visible year-round using satellite-derived sea surface temperature (SST). Analysis of a 41 year (1973-2013) time series of mean monthly frontal positions, determined from weekly, satellite-derived SST charts and digitized at Bedford Institute of Oceanography along 26 longitude lines between 75° and 50°W, allows an examination of inter-annual variability (IAV) of frontal location along each line of longitude. After removing seasonal variability of the front at each longitude by subtracting a 41-year (1973-2013) mean monthly frontal position climatology, IAV of the front's position at each longitude was computed as the annual mean of all monthly position anomalies for each year over the 41-year period. Despite some missing data located largely east of 60° W, a longitude-time plot reveals alternating bands of westward propagating annual mean anomaly values, exhibiting a period of about 10 years (offshore: late-1970s, late-1980s, late-1990s, late-2000s; onshore: early 1970s, early 1980s, early 1990s, early 2000s). Annual mean frontal anomalies are largest in the east, with maxima of O (±100 km) located east of 60° W for years when data are available. Empirical orthogonal function (EOF) modes 1-3 account for ~80% of the variance and are used to form a set of basis functions that describe the frontal anomaly data, allowing reconstruction of the entire data set since missing data are relatively few (8.7%). Data from the Middle Atlantic Bight showing a close correspondence between IAV of frontal position and IAV of both shelf water volume and salinity suggests that the shelf break frontal position may be a useful indicator of changes in shelf water volume and salinity that originate from arctic sources on annual to inter-annual time scales.

Climate-driven changes in oxygen inventories of North Atlantic Subtropical Underwater captured by oceanographic time-series stations

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Historical observations of potential temperature (q), salinity (*S*), and dissolved oxygen concentrations (O_2) in the subtropical North Atlantic (0 – 500 m; 0 – 40° N, 10 – 80° W) were examined to understand changes in O_2 and apparent oxygen utilization (AOU) in Subtropical Underwater (STUW) since the early 20th century. North Atlantic STUW is observed at three of the longest ocean biogeochemical and ecological time series stations in the North Atlantic, namely the CARIACO Ocean Time-Series (10.5°N, 64.4°W), the Bermuda Atlantic Time-series Study (BATS; 31.7°N, 64.2°W), and the European Station for Time-series in the Ocean, Canary Islands (ESTOC; 29.2°N, 15.5°W). STUW is a high salinity (> 35.6) water mass that forms in the surface eastern Subtropical North Atlantic near ESTOC. It reaches BATS and CARIACO in the western half of the North Atlantic

gyre, moving along the $26s_q$ density surface. Since the 1990's, STUW O_2 at CARIACO and BATS has decreased approximately 0.61 and 0.26 μmol kg^{-1} yr^{-1}, respectively. No apparent change in STUW O_2 was observed at ESTOC over this period. This is likely because this location is located to the east of the main STUW formation region, and thus the hydrography at the ESTOC site experiences alternating effects from gyre circulation and from the African upwelling system depending on season and interannual variations. STUW is detected at ESTOC typically in summer and fall, when the trade winds are weaker and the inner Subtropical Gyre expands to the east. Data archived by NOAA NODC show that STUW O_2 has declined 0.76 μmol kg^{-1} yr^{-1} in the eastern Caribbean Sea (10 – 20°N, 60 – 70°W), 0.72 μmol kg^{-1} yr^{-1} the western subtropical North Atlantic (25 – 40°N, 50 – 70°W), and 0.80 μmol kg^{-1} yr^{-1} in the eastern subtropical North Atlantic (20 – 35°N, 20 – 40°W) since the mid-1990. 18 ± 10% of this STUW O_2 loss (19.9 ± 6.3 μmol kg^{-1}) can be attributed to decreased O_2 solubility associated with a ~1 °C increase in sea surface temperature in the formation region of STUW and a 0.045 increase in the mean STUW *S*. However, no significant trend in air-ocean equilibrium O_2 (O_2^{equil}) was detected in STUW during this period. Most of the observed STUW O_2 loss thus seems to be controlled by shifts in ventilation, transport and biological processes (i.e., AOU), rather than changes in diffusive air-sea O_2 gas exchange. A significant positive correlation between the mean annual North Atlantic Oscillation (NAO) index and STUW O_2 ($R^2 = 0.23$, $p < 0.001$) suggests that shifts in wind patterns in the North Atlantic (i.e., westerlies and trade winds) are a dominant control on the STUW O_2 inventory. The positive NAO phase leads to stronger trade winds between 10°N and 30°N. These conditions stimulate the formation of STUW. The observed decreasing trend in STUW O_2 could therefore reflect the NAO shift from its strongly positive phase between mid-1980 and mid-1990 to its neutral or negative phase since the mid-1990 until the present. A lower O_2 decrease rate at BATS (0.26 μmol kg^{-1} yr^{-1}), compared to that of the broader western North Atlantic gyre (0.72 μmol kg^{-1} yr^{-1}), may reflect the strengthening of the westerlies around BATS, and thus ventilation of STUW here, during the current negative NAO phase. We conclude that NAO-driven shifts in STUW ventilation and transport control the STUW O_2 pool, and that changes STUW O_2 associated with climate variability are captured at CARIACO and BATS time series stations.

Ocean Time-Series and the Biological Pump (Monday, 7/21)

Elemental composition (C, N and P) of sinking and suspended particulate matter in the Cariaco Basin, Venezuela

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The elemental stoichiometry [organic carbon (C): nitrogen (N): organic phosphorus (P)] of suspended and sinking particles was examined in samples collected from the Cariaco Basin, Venezuela. Since November 1995, suspended material has been collected each month using Niskin bottles between the surface and 1300 m (suspended P measurements began in 2008) and moored sediment traps (150 (deployed in 2004), 225, 410, 800, and 1200 m) have been used to capture sinking particles. While suspended particle concentrations increase during upwelling periods, suspended N:P molar ratios are similar throughout the year at ~ 40. In contrast, N:P molar ratios of sinking particles collected in the shallowest sediment trap (~150 m depth) are close to Redfield (average of 13.0 during upwelling and 17.8 during non-upwelling), with most of the depth increase in N:P ratios occurring within the upper 230 m, or the oxic portion of the water column. Differences in particulate elemental ratios suggest a predominance of detrital material in the suspended pool, while the sinking particulates have fresher, biologically-derived organic matter. Seasonal changes in the biological community structure are not reflected in the N:P ratios of either suspended or sinking material in the upper 150 m. Rather, differences are apparent in the larger and more rapid increase in the N:P ratio with increasing trap depth during upwelling (~29) versus nonupwelling periods (~19). We argue that sinking organic matter produced during upwelling is more labile and easily remineralized by a biological community primed to respond to episodic pulses in sinking organic matter. Since 2008, the average N:P ratios of suspended matter in the upper 100 m of the water column increased markedly, from ~ 32 to ~ 40, as a result of a rapid decline in the P inventory. During this time frame there was a reduction in diatom abundance and an increase in coccolithophorid, cyanobacteria, and cryptophyte species, coincident with a decrease in upwelling intensity. The suspended N:P ratios are therefore consistent with the observed change in foodweb dynamics and are similar to those observed in other oligotrophic regimes, e.g. Station ALOHA. The lack of a similar increase in sinking particulate N:P ratios throughout the time series is more puzzling. We hypothesize that this may be due to a combination of a long term increase in mesozooplankton and to a change in the composition of sinking organic matter associated with the shift in plankton community structure.

***Prochlorococcus* through the lens of time-series studies: Temporal dynamics of ecotypes and nitrate utilizing genotypes in the Pacific and Atlantic Oceans**

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Prochlorococcus is the numerically dominant phototroph in the oligotrophic subtropical ocean and carries out a significant fraction of marine primary productivity. As a key part of the marine food web, the productivity of *Prochlorococcus* is an important determinant of the fate of carbon in the open ocean. Time-series studies, such as the Hawai'i Ocean

Time-series (HOT) and the Bermuda Atlantic Time-series Study (BATS), have proven instrumental in understanding both the spatial and temporal dynamics of *Prochlorococcus* populations as well as the selection pressures that have shaped them. This group is composed of several polyphyletic low-light (LL) adapted clades (LLI-LLVII) and a more recently diverged group of monophyletic high-light (HL) adapted clades (HLI-HLVI). Analysis of the abundance of five clades (HLI, HLII, LLI, LLII-III, and LLIV) across a 5-year period (2003 – 2007) in the Pacific and Atlantic Oceans has revealed reproducible patterns in their vertical and seasonal distribution in relation to light and temperature variation. Greater water column stability at the Pacific site appears to promote consistent layered distributions of ecotype-populations, while strong seasonal fluctuations at the Atlantic site yield annual succession patterns of populations in response to winter mixing and summer stratification of the water column. These patterns correlate with the known light and temperature optima of cultured isolates.

Selection of particular lineages within clades in response to nutrient availability can also be observed in the Pacific and Atlantic. While most cultured *Prochlorococcus* are incapable of using nitrate as a nitrogen source, some cells within the high-light adapted HLII clade and the low-light adapted LLI clade are known to possess the genes required for nitrate assimilation. Measuring the abundance of the *Prochlorococcus* nitrate reductase gene (*narB*) as a proxy for the nitrate assimilation trait across 2 seasonal cycles (late 2005 – 2007) at HOT and BATS, has revealed patterns of selection that are likely due to nitrogen availability. At BATS, approximately 30-50% of HLII clade cells were estimated to contain *narB* when the water column was stratified and total inorganic nitrogen concentrations were low. This subpopulation declined to <10% of total HLII clade cells following deep winter mixing events that transport nutrients to the surface. In contrast, the HOT site supported a relatively stable subpopulation of HLII clade cells containing the *narB* gene (~20-50%) in the nitrogen poor surface layer. The LLI *narB* gene was found coincident with LLI populations, in higher abundance at BATS, and close to the nitracline. These data show that a significant fraction of *Prochlorococcus* have the capacity to utilize nitrate and highlight ecological differences between distinct phylogenetic groups of *Prochlorococcus* regarding selective pressures that control the distribution of functional traits in wild populations. They add to the evidence that both deeply rooted diversity (e.g. along dimensions of light and temperature) as well as fine-scale diversity (e.g. functional traits and phage resistance) contribute to the stability and resiliency of *Prochlorococcus* populations in the environment.

Wind and solar radiation drive microbial community diversity in the North Pacific Subtropical Gyre

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Time series studies are critical for documenting environmental variation, and relating that to structural and functional variability in biological communities. Here we report a time series study of microbial community variability focused on the Hawaii Ocean Time-series station ALOHA, a perennially thermally stratified site that undergoes mild climatic variation characteristic of the North Pacific Subtropical Gyre (NPSG). Two indicators of microbial diversity (ribosomal RNA amplicon tag sequences and shotgun metagenomic sequences), suggested few strong correlations between community variability at 25 and 500 m depth and 24 different physical and chemical environmental properties. Microbial diversity at 25 m was however positively correlated with the average wind speed of days prior to sample collection. Additionally, microbial community composition at this depth exhibited significant seasonality, through correlations with solar irradiance. Many of the same microbial taxa whose relative abundances appeared influenced by changes in solar radiation at Station ALOHA, also demonstrate dramatic seasonality in other parts of the ocean. At 500 m, microbial communities were less variable and exhibited no clear relationships to fluctuations in measured environmental properties. Due to relatively mild seasonal variation in habitats like the NPSG, episodic wind events appear to be a major driver of surface water microbial diversity. In contrast, overall seasonal community composition in NPSG surface waters varied in a similar way but in a less dramatic fashion as in other oceanic regions. Near-surface microbial community variation at 25 m appeared to have minimal impact on the upper mesopelagic at 500 m, where microbial communities were more stable.

The Hawaii Ocean Time-Series (HOT) Program: Highlights from more than a quarter century of sustained ocean observations in the subtropical North Pacific

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Since 1988, the Hawaii Ocean Time-series (HOT) program has sustained near-monthly observations at the field site Station ALOHA (22.75°N, 158°W) in the North Pacific Subtropical Gyre. The resulting time-resolved suite of measurements has fundamentally changed our view of ecosystem variability in the open sea. The emergent data highlight connectivity between ocean-climate, plankton ecology, and biogeochemistry over episodic to decadal time scales. The sustained, high quality observations have provided new insights into ocean processes and have highlighted scales of variability in this persistently oligotrophic ecosystem. One reflection of the increasing value of these observations is the continued expansion of science conducted at Station ALOHA, including a diverse set of autonomous and remote sensing platforms and diverse science and education programs. The resulting program measurements continue to contribute to our understanding of long-term trends in ocean carbon inventories and fluxes, quantify temporal variability in nutrient fluxes and inventories, and document the important role of plankton community structure in carbon export to the deep sea. Accessibility of program data through the user-friendly online system (Hawaii Ocean Time-series Data Organization and Graphical System; HOT-DOGS) has facilitated wide use of program data. Moreover, through collaborative and leveraged partnerships, HOT continues to build a strong network of international scientists whose work at Station ALOHA strengthens the utility of the core HOT program measurements.

The Oceanic Flux Program (OFP) time-series of particle flux in the deep Sargasso Sea: Linkages with upper ocean physics and biology

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The Oceanic Flux Program (OFP) time-series off Bermuda has produced an unequalled, nearly continuous, high resolution record of particle flux in the deep Sargasso Sea that spans more than 35 years. The OFP time-series, in conjunction with the co-located BATS and (former) BTM time-series, has provided key data in which to assess how seasonal and non-seasonal variability in the deep ocean flux is linked with physical and biological forcing and with climate variability. The record length of the OFP time-series allows us to statistically describe how the particle flux for any period in the seasonal cycle relates to its expected magnitude, based on the long-term flux climatology. Inter-annual variability in deep water particle flux is greatest during the transitional seasons of early winter and late spring, when surface stratification is weak and the influence of mesoscale physical variability most pronounced. In addition to biological phenomena (e.g. salp blooms), transient meso-scale features, such as passage of productive eddies which alter upper ocean mixing and export characteristics, can generate short-lived pulses of high fluxes of labile material to the deep ocean. However, not all productive eddies passing over the site affect the deep flux similarly, underscoring the importance of physics and ecosystem structure on the coupling between surface ocean productivity and export flux, and of particle recycling in the ocean interior by mesopelagic ecosystems. Causative processes that influence this coupling can be identified through detailed examination of organic and inorganic flux components.

Predator-prey relationships and their link to carbon export at the Bermuda Atlantic Time-Series Station

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In oligotrophic oceans, such as the Sargasso Sea, pico and nanoeukaryotes collectively dominate primary production but their utilization by larger zooplankton, which ultimately determines their role in carbon export, is still unclear. Despite its high seasonal variability, phytoplankton biomass in the Sargasso Sea is low throughout most of the year and is thought to be micrograzer controlled. The overall goal of this study is to investigate the trophic dynamics within the microbial loop and the impact on carbon export in the Sargasso Sea. We hypothesize that a less micrograzer-controlled system leaves some pico and nanophytoplankton to form aggregates or to be grazed by larger zooplankton, which through their fast-sinking fecal pellets facilitate higher particulate export. We investigated growth and grazing rates, applying the dilution method *in situ*, and the taxonomic composition of the eukaryotic and cyanobacterial community at the Bermuda Atlantic Time-series Study station (31'40°N 64'10°W) in July 2012. We also collected and analyzed particulate matter from sediment traps at 150 m to investigate the contribution of the eukaryotic and cyanobacterial community to the sinking flux using 454 pyrosequencing. Changes in the community during incubations were measured by epifluoresence microscopy, flow cytometry and quantitative Polymerase Chain Reaction (specific for Mamiellales, an order within the prasinophytes). Our results showed that the microzooplankton grazing rates were high on all phytoplankton groups, tightly controlling the phytoplankton production. We hypothesize that this coupling likely leads towards recycling of carbon within the euphotic zone instead of carbon export, however the trap material shows the presence of pico and nano euks such as Haptophyceae and *Prochlorococcus*, suggesting other pathways for the export of carbon. We also show in this study how different molecular techniques can be combined to calculate taxon specific growth and grazing rates of the community and its relative contribution to water column production and carbon export.

Numerical modeling and remote sensing studies of regional marine biogeophysical variability around the Hawaii Ocean Time-Series (HOT) station ALOHA

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We characterize the marine biogeophysical variability in the region around the Hawaii Ocean Time-Series (HOT) station ALOHA using a hierarchy of numerical modeling and satellite remote sensing approaches. Illustrated tools include: 1-D vertical simulations with assimilation of HOT time-series and glider physical data; nested high-resolution 3-D biophysical simulations; and geostatistical and seascapes analyses of satellite ocean color imagery. The results indicate how eddy dynamics generate substantial (sub-)mesoscale biogeophysical variability on synoptic timescales that overlays lower-frequency seasonal and interannual variability.

Time-series investigations of settling particle flux and composition in the deep Canada Basin, Arctic Ocean

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The objective of this research is to clarify the characteristics of the biological pump (i.e., functionality) in the central Canada Basin by examining the export of particulate organic carbon (POC) and other components to the deep basin. As a result of prior biogeochemical investigations, it has been established that biological pump processes in the cryopelagic Arctic Ocean are – presently – unique among major ocean basins with regard to functionality and particle provenance (i.e., allochthonous vs. autochthonous inputs) as a consequence of the dominant role of sea ice conditions, hydrography and land-locked nature of the basin. How will this "cryogenic mediterranean ocean" respond to changing environmental conditions, and how it will impact the global carbon cycle? These are major unanswered questions that provide strong motivation for our investigation.

To address these questions, we have established a biogeochemical flux program within the framework of the Beaufort Gyre Observing System (BGOS) program in the deep Canada Basin that provided information on settling particles obtained from time-series sediment trap samples collected over 4 years at different depths and locations in the deep basin resulting in the following key observations. First, with respect to *functionality of particle supply to the deep basin*, (*i*) very low particle fluxes relative to other ocean basins are indicative of a weak biological pump (*ii*) seasonal variations in mass flux, which are dominated (~80%) by lithogenic material, are highest during maximum ice coverage at all locations; (*iii*) Annual integrated mass fluxes decrease towards the interior of the Basin, while concentrations of POC and PIC increase and Al (lithogenic component) concentrations decrease; *(iv)* Nd isotope analyses indicate at least 2 sources of allochthonous lithogenic material detected at all quadrants of the basin and, along with C isotopes provide constraints on particle source; Finally, (*v*) a marked increase in mass flux coincident with the 2008 Minimum Ice Condition was due to an increase in allochthonous input, and not to an increase in vertical export production.

The particle flux observations obtained on the time-series samples acquired and measured thus far suggest that the marked changes in surface conditions have not – as of yet - propagated to the deep Basin. It is vital to distinguish between and anticipate scenarios of a perennially weak biological pump, and gradual shift in strength, or an abrupt shift in mode and intensity. In this context, understanding [changes in] Arctic Ocean biological pump processes are crucial for our understanding of large-scale changes in ocean biogeochemistry and their impacts on the global carbon cycle.

Interpretation of particulate carbon flux data from bio-optical profiling floats at BATS

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A mechanistic understanding of the ocean biological pump is limited by lack of carbon flux observations from the upper kilometer of the ocean. Development of autonomous sensors for particulate carbon (PC) flux could transformatively expand the number of available measurements. Transmissometers on autonomous profiling floats serve this purpose qualitatively as "optical sediment traps". Here we interpret optical proxy observations in the context of 1) field measurements of PC flux and flux size distribution collected with co-deployed, transmissometer-equipped, neutrally-buoyant sediment traps (NBSTs), and 2) laboratory calibrations with model particles. Field data were collected during a series of 5 cruises at the Bermuda Atlantic Timeseries Study (BATS) site. We compare direct PC fluxes (from NBST samples) to simultaneously-observed, proxy measurements (from transmissometers used as "optical sediment traps"). The resulting data set provides a preliminary calibration of the autonomous, optical carbon flux proxy and sheds light on possible sources of variability in sensor response. Our observations also illustrate high spatiotemporal resolution variability in particulate carbon flux at BATS.

Characterizing variability: The benefits of long-term monitoring in Narragansett Bay 1959-2014

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Narragansett Bay, Rhode Island, is a highly productive and dynamic estuary with annual rates of primary production (220-440 gC m^{-2} yr^{-1}) similar to George's Bank and about four times that of the North Sea. Seasonally, temperatures in Narragansett Bay range from -1.5 to 25 °C and N and P concentrations range from 0-28 μM and 0-2 μM, respectively. Here, we will give an overview of the Narragansett Bay long-term plankton time series, initiated by T. Smayda. It is the world's longest-running plankton time series, with weekly counts of phytoplankton species composition conducted since 1959. This unique time series has led to several insights into physical and biological variability of the Narragansett Bay estuary, including long-term changes in water temperature, phytoplankton species composition, chlorophyll a concentrations and bloom timing.

Microbial community structure and function on sinking particles at station ALOHA

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Marine microbes play critical roles in the cycling of carbon and energy through our biosphere yet their roles in processing sinking particles, a major component of the biological pump, are still only poorly understood. The main goal of this study was to better define the microbial taxa and biochemical processes involved in carbon and energy cycling on sinking particles collected at different depths in the North Pacific Subtropical Gyre at station ALOHA. We used metagenomic approaches to compare microbial communities associated with sinking particles, collected using sediment traps at four depths between 150 meters and 500 meters during 2012 and 2013, with free-living microbes collected at the same depths. Across all studied depths, there was a pronounced enrichment of *Alteromonas* and other organic-matter degrading species in "live" traps in which microbial growth and processing continued until trap recovery. In contrast, "dead" traps containing fixative were dominated by known eukaryote-associated bacterial taxa including *Vibrio* and *Arcobacter* and by chemoautotrophic taxa such as *Sulfurospirillum*, *Sulfurovum* and *Sulfurimonas*. Euryarchaeota and Thaumarchaeota were the most abundant Archaeal phyla in traps and seawater samples and exhibited contrasting depth-specific trends in abundance in both live traps and seawater samples. Notably, these trends overlie more complex taxa-specific depth patterns within each phylum. Metagenomic analyses of microbes associated with sinking particles revealed the diversity and functional attributes of microbes on sinking particles, and provide new insight into this important component of the marine carbon cycle.

HOT-DOGS: A user friendly graphical interface to access and retrieve Hawaii Ocean Time-series program data

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The Hawaii Ocean Time-series (HOT) study is an ongoing, 26-year ocean observation program with a large growing database of biogeochemical and physical measurements. On approximately monthly intervals since October 1988, a multidisciplinary suite of environmental measurements have been conducted from the HOT field site Station ALOHA (22°45´N, 158°W); all HOT data are freely accessible via servers at the University of Hawaii (http://hahana.soest.hawaii.edu/hot/hot_jgofs.html and (http://www.soest.hawaii.edu/HOT_WOCE) and from BCO-DMO (http://www.bco-dmo.org/project/2101). In order to make these data sets fully available and interactive, HOT developed a user-friendly interface called Hawaii Ocean Time-series Data Organization and Graphical System (HOT-DOGS).

Independent modules facilitate: (1) data extraction to obtain a text file consisting of one or more data columns, (2) data display to plot selected variables, (3) comparisons of a selected data set, or depth-integral thereof, in time, (4) time-series analyses and contour plots of data grouped by depth, potential density or temperature. This user-friendly

interface has proven invaluable for both research and teaching applications, and has greatly facilitated wide use of HOT program data.

Coupling O_2/Ar and triple oxygen isotope distribution with estimates of vertical transport to constrain biological production in the coastal ocean

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In the last decade, O_2/Ar ratios and the triple oxygen isotope composition (TOI) of dissolved O_2 has been measured in many regions to simultaneously estimate net (NOP) and gross oxygen production (GOP) in the surface ocean. Both of these can be stoichiometrically related to carbon production and therfore, the NOP/GOP ratio reflects the efficiency of an ecosystem to export, rather than recycle, organic carbon. This approach has been limited in regions with strong vertical transport because transport estimates are often difficult to determine and seldom made in oxygen-based studies. This is especially an issue when the majority of biological production occurs beneath the surface mixed layer. In this study, we combine profiles of the concentration and isotopic composition of oxygen with concurrent estimates of upwelling velocity and eddy diffusivity, based on a mass balance for ^{7}Be ($t_{1/2}$=53d) and wind-based estimates of turbulent kinetic energy dissipation. Mass balances for oxygen are based on a 1-D, non-steady state, two-box model of the upper ocean at the San Pedro Ocean Time-series (SPOT) in Southern California, with observations of both tracers at ~two week intervals used to constrain model parameters. During Spring 2013, upwelling velocities ranged from 0.6 to 2.8 m d^{-1} at SPOT, delivering nutrients which supported GOP rates of 184 to 783 mmol m^{-2} d^{-1} and NOP rates of up to 189 mmol m^{-2} d^{-1}, which translates to Net Community Production (NCP) in the euphotic zone of up to 135 mmolC m^{-2} d^{-1}. NOP/GOP ratios in the euphotic zone reached up to 0.48 and peaked prior to the maximum in upwelling velocity and GOP. Organic carbon export during spring months, measured in sediment traps set at 100m combined with a water column ^{234}Th budget, ranged from 3.3 to 21.4 mmolC m^{-2} d^{-1}. Export followed a temporal trend similar to NCP in the euphotic zone, but were ~5x smaller due to remineralization above the traps. Our results show that it is possible to apply the dissolved O_2/Ar and TOI tracer pair to estimate production rates along the ocean margins, and that the export efficiency of this ecosystem changes over time.

Observations of net community production by Argo floats

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Net community production (NCP) in the upper ocean is a crucial factor in the rate of particulate organic carbon export to depth and ultimately an important constraint on atmospheric CO_2. In this study we use a global set of Argo floats equipped with oxygen sensors to determine the rate of NCP in the seasonal pycnocline (i.e. below the mixed layer depth). The floats profile nominally once every 5-10 days, with oxygen sampled vertically every several meters in the upper ocean. The vertical and temporal density of oxygen measurements allow us to estimate NCP as a function of depth at several different geographic regions. Argo derived NCP profiles compare favorably to NCP determined from time-series at Hawaii and Bermuda. We also find moderate correlation between NCP calculated from Argo and net primary production from satellite data.

Variability in particle export at Station ALOHA

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The biological carbon pump links the atmospheric and deep-sea reservoirs of carbon via primary production, particle export and organic matter remineralization. Since Dec 1988 we have measured particle export from the euphotic zone (150 m) at Station ALOHA using sediment traps deployed for ~3 days on approximately monthly intervals. For selected periods, we have also measured particle fluxes at multiple reference depths throughout the upper mesopelagic zone (150-750 m). Particulate carbon and nitrogen (PC and PN, respectively) fluxes were coupled and exhibited both seasonal and subdecadal scale variability. PC export at 150 m averaged 2.2 mmol C m^{-2} d^{-1} and ranged from 2-15% of euphotic zone depth-integrated primary production (^{14}C-based). The temporal pattern of particulate phosphorus (PP) flux was decoupled from PC and PN fluxes, and exhibited a systematic decrease over the 25-yr observation period; molar PN:PP export ratios have more than doubled since 1988 to current values in excess of 40:1. This change in the stoichiometry of the exported particles is hypothesized to be a consequence of enhanced nitrogen fixation, which currently supports more than 50% of the new production at Station ALOHA.

The Bermuda Atlantic Time-Series Study: Sustained physical, biogeochemical, ecosystem, and ocean change observations and linkages in the subtropical North Atlantic

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The Bermuda Atlantic Time-series Study (BATS) program has sampled the northwestern Sargasso Sea on a biweekly (January to April) to monthly basis since October 1988. The primary objectives of the BATS program continue to be an improved understanding of the biological, chemical and physical mechanisms that control the biogeochemical cycling of carbon and related elements in the surface ocean and their export to the ocean interior. With 24 years of measurements for most chemical, physical and biological variables, we have moved beyond descriptions of seasonal and interannual variability to examination of multi-year trends and potential controls, however there remain substantial gaps in our knowledge of the ecosystem mechanisms related to organic matter production, remineralization and export. For example, what mechanisms support the seasonal drawdown of carbon dioxide in the absence of detectable nutrients? What are the ecosystem pathways that result in the discrepancy between biological (i.e., sediment trap) and geochemical (e.g., oxygen based NCP) estimates of carbon export production? Does the elevated nitrate to phosphate ratio in the seasonal thermocline (N:P > 30 on average) result from local production and remineralization processes or upstream processes? What is the interplay between convection and eddy dynamics as it impacts the mixed layer depth, nutrient inputs and ecosystem productivity? For each of these questions we possess significant understanding through BATS core and ancillary datasets. For example, we know that small eukaryotic phytoplankton during the summer stratified period can access the deep nitrate pool and thus contribute to net carbon drawdown. We know that zooplankton, particularly the vertical migrators, are increasing and thus enhancing the active flux of particulate organic carbon to the ocean interior. We now know that phytoplankton production and subsequent export by small phytoplankton does not occur in Redfield proportions thus contributing to non-Redfield behavior in the nutrient fields. We have observed that cyclonic eddies reinforce mixing and can lead to spectacular open ocean phytoplankton blooms. We present a mini-review of the current state of knowledge of each of these questions at BATS and highlight areas for further scientific inquiry.

An integrated observation system of biogeochemical time-series

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Changes in primary production and/or carbon export from the euphotic zone to the deep can have significant impacts on the biological pump, which in turn has implications for the removal of carbon dioxide from the atmosphere on long time-scales. Thus, understanding how the biological pump will respond to the changing climate is a research priority world-wide. Ocean carbon sources and sinks are controlled by physical and biological processes that act at various temporal and spatial scales. Identifying shifts in marine ecosystems, and their impacts on carbon export, requires continuous, high quality observations. Time series of ocean biogeochemistry and ecological observations play a critical role in documenting and evaluating mechanisms of how marine ecosystems respond to changes in climate. Time-series studies have already clearly demonstrated interannual to decadal-scale variability in ocean biogeochemical processes. There are over 160 ship-based biogeochemical time-series around the world, which take a wide range of measurements at a variety of time-scales necessary to understand changes in the biological pump. These time-series constitute the building blocks of a true international global biogeochemical ocean monitoring program. Many of these time-series are located in continental margins, which play a fundamental role in ocean biogeochemical cycles and carbon export, and are biologically and geochemically active areas of the biosphere, exchanging large amounts of material with the open oceans. However, strong support by the scientific community and long-term commitment by nations is required to maintain these critical ocean observation systems. Here we present information on the most recent biogeochemical time-series activities, such as the International Time-Series Network (http://www.whoi.edu/website/TS-network/home; http://www.unesco.org/new/en/natural-sciences/ioc-oceans/sections-and-programmes/ocean-sciences/biogeochemical-time-series/) and the International Group for Marine Ecological Time Series (IGMETS; http://www.igmets.net/). By pooling together time-series resources, it will be possible to compile an assessment of changing biogeochemistry and ecosystem dynamics at a global scale.

The CARIACO Ocean Time-Series: 19 years of international collaboration in ocean biogeochemistry and ecological research

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The CARIACO Ocean Time-Series seeks to establish a comprehensive understanding of the complex interactions that occur between hydrography, food web dynamics and biogeochemistry, and how variation in these processes are preserved in sediments accumulating in the underlying anoxic sediments. CARIACO serves the ocean carbon and biogeochemistry, ocean ecology and biodiversity, and paleoclimate research communities by maintaining an observation framework for studying variability and trends in ocean biogeochemistry and ecology spanning monthly to millennial time scales. The CARIACO Program is now a nexus of communication and model for other ocean observing programs in Central and South America. It is a community facility platform, open for use by other physical and biogeochemical programs. The CARIACO Ocean

Time-Series owes its success to the strong collaborations between scientists in Latin America, the US, and other countries. All of the data generated by the program are openly available to the broader community. Over 110 publications have been produced using this platform by members of the broader research community using these data.

The CARIACO program has contributed to our knowledge of decomposition and recycling of particles as part of the biological pump. It has added to our understanding of oxygen minimum zones and of anoxic biogeochemistry processes in the ocean. In the upper 100 m of the water column, flux of biogenic particles is closely coupled with phytoplankton biomass and productivity. However, this relationship disappears below the euphotic zone. Vertical particulate organic C (POC) fluxes in the upper 100 m are an order of magnitude higher than those measured using moored sediment traps at 225 m. Despite this basin being anoxic below ~250m, remineralization rates of organic matter are comparable to those in well oxygenated waters. Over the past 19 years, POC fluxes measured throughout the water column using sediment traps have varied in response to changes in surface Chl-*a* concentrations and phytoplankton community composition. In turn, these changes are related to long-term variations over much larger spatial scales spanning the entire tropical Atlantic Ocean. The observations of CARIACO are critical for better understanding the biological pump on upwelling-dominated continental margins. The knowledge gained through this facility helps to understand impacts of present climate change on carbon sequestration efficiency. The time series also serves the paleoclimate community as the sediments accumulating in the Cariaco Basin provide one of the best marine archives for reconstructing past climate change.

Sinking velocities and microbial respiration rates alter the transfer efficiencies of particulate carbon fluxes through the mesopelagic zone

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The attenuation of sinking particle fluxes through the mesopelagic zone is an important process that controls the sequestration of carbon and the distribution of other elements throughout the oceans. Case studies at two contrasting sites, the oligotrophic regime of the Bermuda Atlantic Time Series (BATS) and the mesotrophic waters of the western Antarctic Peninsula (WAP) sector of the Southern Ocean, revealed large differences in the rates of particle-attached microbial respiration and the average sinking velocities of marine particles, two parameters that affect the transfer efficiency of particulate matter from the base of the euphotic zone into the deep ocean. Rapid average sinking velocities of 270 ± 150 m d^{-1} were observed along the WAP, whereas the average velocity was 49 ± 25 m d^{-1} at the BATS site. Respiration rates of particle-attached microbes were measured using novel RESPIRE (REspiration of Sinking Particles In the subsuRface ocEan) sediment traps that first intercepts sinking particles then incubates them in situ. RESIRE experiments yielded flux-normalized respiration rates of 0.4 ± 0.1 d^{-1} at BATS when excluding an outlier of 1.52 d^{-1}, while these rates were undetectable along the WAP (0.01 ± 0.02 d^{-1}). At BATS, flux-normalized respiration rates decreased exponentially with respect to depth below the euphotic zone with a 75% reduction between the 150 and 500 m depths. These findings provide quantitative and mechanistic insights into the process that control the transfer efficiency of particle flux through the mesopelagic and its variability throughout the global oceans.

Rates of primary production and organic carbon export at HOT

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Primary production (PP) rates were estimated using concurrent ^{14}C and ^{18}O bottle incubations and a non-incubation oxygen isotope ($^{17}\Delta$) based method during monthly cruises to the time-series station ALOHA in the subtropical N. Pacific Ocean between March, 2006 and February, 2008. The mean gross oxygen production (GOP) rate in the photic layer (0-200m) at ALOHA was estimated at 103±43 and 78±17 mmol O_2 m^{-2} d^{-1} from the $^{17}\Delta$ and ^{18}O methods, respectively. In comparison, the mean ^{14}C-PP rate (daytime incubations) in the photic layer was 42±7 mmol C m^{-2} d^{-1} (502±84 mg C m^{-2} d^{-1}). The ratio of ^{18}O-GOP/^{14}C-PP decreased with depth from ~2.5 at the surface to ~1 at 100m. GOP rates measured using the non-incubation $^{17}\Delta$ method exceeded the ^{18}O incubation method by 25-60%, which likely results from methodological biases. A supersaturation of the dissolved O_2/Ar gas ratio was measured at HOT in the surface layer every month yielding a mean annual value of 101.3±0.1% and indicating a consistent net autotrophic condition. The mean annual net community production (NCP) rate at ALOHA estimated from dissolved O_2/Ar gas ratio was 14±4 mmol O_2 m^{-2} d^{-1} (120±33 mg C m^{-2} d^{-1} or 3.7±1.0 mol C m^{-2} yr^{-1}) for the mixed layer. A NCP/GOP ratio of 0.19±0.08 determined from $^{17}\Delta$ and O_2/Ar measurements indicated that ~20% of gross photosynthetic production was available for export and harvest from the mixed layer.

Nitrification as a tracer of particle flux and remineralization in the twilight zone of the Northeast Pacific Ocean

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The first and rate-limiting step of nitrification is the oxidation of ammonia to nitrite (ammonia oxidation). This means that the rate at which nitrification occurs in the ocean is largely constrained by the flux of ammonium, via the remineralization of organic matter. In the dark ocean, this flux is directly related to how much organic material escapes the euphotic zone, the rate at which the nitrogen it contains is returned to dissolved form, and

how this rate changes with depth. We wanted to know if nitrification rates decrease with depth in the dark ocean according to a power-law function, and how closely the fit, in terms of carbon, relates to the flux equation put forth by Martin from data collected during VERTEX.

When we analyzed nitrification rate data obtained during several cruises along CalCOFI lines 60 and 67 in the NE Pacific Ocean, we confirmed that nitrification rates decline with depth below the euphotic zone (50 – 1000 m) according to a power-law function. In carbon equivalents, an export flux of 106 g C m^{-2} yr^{-1} is required to support the nitrification rates observed in the upper 1000 m of the NE Pacific Ocean. In their carbon budget for the region, Pennington & Chavez estimated new primary production in the central CCS to be 169 g C m^{-2} yr^{-1}, of which 93 g C m^{-2} yr^{-1} are expected to sink below the euphotic zone. The striking agreement between annual export flux estimates introduces the potential to use depth-integrated nitrification rate measurements to study spatiotemporal variability in carbon export and remineralization in the upper 1000 m of the dark ocean.

Nitrification rates measured at different stations/times were more consistent within an isopycnal than they were at given depth interval. The isopycnal bearing the highest nitrification rates is also where the highest concentrations of nitrite and ammonium occur, as well as an excess of nitrate relative to silica. Analysis of 1 m resolution downcast data from repeat hydrography cruises in the region shows this ‘nitrification zone’ to be positioned within the steepest part of the pycnocline, a place where the sinking rate of particles is believed to slow, increasing the time that they are exposed to decomposition and remineralization. Meaning, it may represent the zone where remineralization rates are highest and most variable. The positioning of this zone just below the deep chlorophyll maximum also suggests that the rate of nitrification/remineralization in this zone has immediate effects on the amount of N that enters the euphotic zone.

Plankton time series at the Martha’s Vineyard Coastal Observatory

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Interdisciplinary time series observations have unique potential to provide insights into the ways environmental change is influencing the structure and function of coastal ocean ecosystems. We are taking advantage of new in situ observing technologies combined with the capabilities of the Martha’s Vineyard Coastal Observatory (MVCO) to focus on processes over the inner shelf off the northeast coast of the US. Our approach depends on hydrographic and meteorological observations coupled with high resolution (~hourly) multi-year time series of taxonomically resolved phytoplankton acquired with FlowCytobot (FCB) and Imaging FlowCytobot (IFCB). FCB and IFCB are automated submersible flow cytometers optimized for measurement of picoplankton and microplankton, respectively. Results from these on-going time series (FCB since 2003, IFCB since 2006) emphasize dramatic seasonality in community structure, distinct taxon-specific interannual variations, and significant multi-year trends that may be associated with long-term warming. Picocyanobacteria, for instance, are most abundant in summer and have been increasing in biomass over the last decade. In contrast, the microphytoplankton, which are dominated by diatoms, typically bloom in fall and winter. Multi-year bloom records indicate that the most important species contributing to diatom biomass is strongly influenced by parasitic infection, with some evidence suggesting infection may increasingly limit blooms as warming trends continue.

Atypical behavior of the biological carbon pump in an oxygen-depleted water column: The Cariaco Basin case study

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The classic paradigm for carbon flux in the ocean is that organic matter is formed in the surface well-lit ocean by photosynthetic organisms, processed by the food web, and remineralized at depth as it sinks, resulting in carbon flux decreasing as a power function of depth (e.g., Pace et al. 1987). In the Cariaco Basin, however, and likely in other coastal, oxygen-depleted regions (OMZs, Black Sea, Baltic Deeps, hypoxic regions), the situation is more complex. Over the past 19 years, the CARIACO Ocean Time Series program has collected data on sinking fluxes, water column geochemistry and microbiology at a site in the deep (1400 m), permanently anoxic Cariaco Basin which underlies a seasonal upwelling zone on the continental margin of Venezuela. At Station CARIACO, organic carbon flux to 225 m often exceeds flux to 150 m (40% of concurrent observations), flux to 410 m exceeds flux to 225 m in 35% of concurrent observations and flux to 800 m exceeds flux to 400 m on 18% of observations. A similar trend was found for flux of the "terrestrial fraction". A persistent and relatively large (0.12-2.0 g C m^{-2} d^{-1}; mean = 0.53) peak in dark carbon fixation rates is typically seen at depths where sulfide appears, a phenomenon which has been observed in most other anoxic basins. Microbiological studies have demonstrated the presence and activity of a variety of chemoautotrophic microorganisms, including thiotrophs, nitrifiers and anammox bacteria. However, the isotopic and biomarker compositions of material collected in traps below this subsurface productivity maximum are not discernibly different from material collected near the surface, suggesting that midwater production may contribute little to excess sinking material. Plausible alternative sources for observed flux anomalies include diagonal transport from more productive waters, active material translocation by migrating zooplankton, and lateral transport of resuspended shallow water coastal sediments. For example, comparisons of N:P ratios in sinking material with rates of accumulation of N and P in deep basin waters suggest the episodic importance of an inorganic P-enriched fraction (Scranton et al 2014) . For this latter mechanism, we hypothesize that shallow coastal sediments resuspended into oxic waters (allowing precipitation of iron oxides with absorbed phosphate) are advected laterally into the central basin between depths of 100 and 400 m. This advective flux may contribute to observed anomalies and provide labile carbon and oxidized iron and sulfur to support dark carbon fixation which cannot be sustained by vertical flux alone. Temporal patterns of pools and fluxes will be explored to evaluate these alternative hypotheses.

Temporal variations in mesozooplankton contributions to export flux at Stn. ALOHA

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Mesozooplankton contribute to the biological pump in two major ways. Their grazing in the euphotic zone transforms and concentrates small particles into larger fecal pellets, which sink passively through the water column. Metabolic and mortality losses from migrating zooplankton also actively move material from surface waters at night to mesopelagic daytime depths. Annual mean biomass of mesozooplankton has increased significantly over 20 years of sampling at Stn. ALOHA and is currently ~0.5 g m^{-2} higher than the initial 3-5 years of observation. This indicates an enhanced role in trophic processes of the upper water column, which is also suggested by the increased amplitude of the seasonal cycle (summer maximum) in recent years. In contrast, migrant biomass has been relatively static, with a slight, but insignificant, temporal trend. Here we use stoichiometric and metabolic assessments to estimate the changing relative contributions of mesozooplankton to cycling and export of carbon, nitrogen and phosphorous at Stn. ALOHA.

Effects of photobleaching on dissolved organic matter bioavailability to bacterioplankton in an upwelling-driven coastal system

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Photobleaching can dramatically alter the bioavailability of dissolved organic matter (DOM) to bacterioplankton in surface waters, yet the nature of this effect varies across systems and study conditions. We will present preliminary results from an ongoing study of the effects of photobleaching on dissolved organic carbon (DOC) bioavailability in the upwelling-driven Santa Barbara Channel, California, USA, a system in which we have measured repeating seasonal patterns in bacterioplankton activity and community composition and DOM accumulation. We will expand on those observations by investigating month-to-month variability in bacterioplankton responses to experimentally

bleached DOM in dilution batch-culture bioassays, using both surface waters, collected on the Plumes and Blooms time-series cruise program, and representative complex DOM compounds (e.g., aged phytoplankton exudates). Over the fall and winter, we saw both decreases and increases in net bacterial production and DOC drawdown after bleaching. This month-to-month variability, over a period of generally oligotrophic conditions, suggests that details of DOM composition will be critical to explaining the effects of photobleaching on the fate of the DOM. We also observed a general convergence of bacterial community composition within bleached samples across multiple months, while unbleached samples developed markedly distinct communities, which we hypothesize to be indicative of a homogenization of the DOM pool due to bleaching. We will relate short- and long-term differences in usage to in situ and remotely sensed parameters and characteristics of DOM composition, with the goal of constraining the effects of photobleaching on DOC cycling in the SBC – that is, whether photobleaching promotes net bioavailability or net persistence of DOC over an annual cycle.

In situ bio-optics and remote sensing of Station ALOHA

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As a core component of the Hawaii Ocean Time-series, the bio-optics program has measured apparent and inherent optical properties of Station ALOHA since 1998. These data include spectra of downwelling irradiance and upwelling radiance, hyperspectral and multispectral absorption and attenuation of particulate and dissolved material, and measurements of particle concentrations and particle size. The temporal resolution of these observations ranges from daily cycles to seasonal and interannual periods. Since 2002, we have paired these data with various regional remote sensing products, including sea surface temperature anomalies, standard chlorophyll products (OC3M) as well as the ocean color index (OCI) algorithm for low level chlorophyll. Here we will present a subset of findings from this rich dataset. Vignettes include time-series of the particle absorption in the upper euphotic zone, the relationship between particle size and primary productivity, diel cycles of particulate carbon derived from beam attenuation and the influence of color dissolved organic material on chlorophyll retrievals from space.

The Biological Pump: Transport Mechanisms and Mesopelagic Processes (Tuesday, 7/22)

Regional and depth-related differences in the capabilities of Arctic microbial communities to degrade organic matter

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Heterotrophic microbes produce extracellular enzymes to hydrolyze substrates to sizes sufficiently small for uptake. The rates of hydrolysis and structural specificities of extracellular enzymes thus determine which substrates are bioavailable. In this study, we compared the enzymatic capabilities of microbial communities from various regions in the Arctic, covering sites and depths not previously investigated, at latitudes from 79°N to 88°N. Seawater samples were collected at four depths in the water column (surface, chl *a* max, 500 m, and bottom water) and incubated with a suite of fluorescently-labeled peptide and polysaccharide substrates to capture the range of substrate specificities of microbial communities. Our results reveal very distinct spatial patterns of peptide and polysaccharide hydrolysis. Depth seems to exert a major influence on peptidase activity: exopeptidases contribute significantly to total peptide hydrolysis rates in the surface waters and decrease with depth. In contrast, the range of hydrolyzed polysaccharides was distinct regionally and with depth, perhaps due to influence of hydrography. These emerging spatial patterns indicate functional variability among Arctic microbial communities, which may be linked to compositional differences due to biogeography of microbial communities.

Dissolved organic phosphorus isolation: Implementation of a bench-top electrodialysis-reverse osmosis unit

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The combination of electrodialysis and reverse osmosis (ED/RO) has shown promise as a novel technique for the isolation of marine dissolved organic matter (DOM). The advantage of the ED/RO technique is the production of a salt-free, concentrated DOM isolate with minimal size-fractionated losses. We have recently designed and constructed a bench-top ED/RO instrument to assist in the examination of the natural distribution and biological production of dissolved organic phosphorus (DOP) using liquid and solid-state ^{31}P NMR. The objective of this study was several fold. 1) Maximize the RO concentration component for DOP isolation. 2) Assess sample integrity using ^{31}P NMR. 3) Determine sample loss through ED phase desalting. 4) Couple ED+RO for method assessment. All representative DOP compound standards (phosphoester, phosphonate, and polyphosphate) were shown to have recoveries of $\geq$90% following a weak alkaline soak (sodium hydroxide, pH 10-11) of the RO membrane. Solid-state ^{31}P-NMR confirmed standard DOP compound integrity for phosphoester and phosphonate compounds, however, polyphosphate underwent hydrolysis during storage. ED-only phase desalting indicates 24% (S.D. = 2.4%) soluble reactive P loss and nearly complete DOP retention when desalted to ~3mS. ED/RO coupled isolation indicates a significant fraction (~22%) of DOP was still adsorbed to the membranes following multiple recovery extractions. Further efforts will optimize ED/RO operating procedures, particularly emphasizing on the optimal extraction method (pH adjustment, solvent compound and

concentration, and storage time) to minimize integrity biases, while maximizing recovery.

A mesoscale eddy natural tracer experiment to investigate N-loss isotope effects off the Peru coast

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Eddies have been identified as important fixed nitrogen (N) loss hotspots in Oxygen Minimum Zones (OMZs), and may significantly impact the global rate of N-loss in OMZs and, ultimately, the global ocean's N isotope budget. As such, they represent 'natural experiments' with intensified biogeochemical signals that can be used for understanding the large-scale processes controlling N-loss. We present the concentrations and N and O isotopic compositions of nitrate (NO_3^-), nitrite (NO_2^-) and biogenic N_2) associated with a coastal anticyclonic eddy in the Peru OMZ observed during two cruises in November and December 2012. Corresponding to the near exhaustion of NO_3^-, we measured the highest $d^{15}N$ values for both NO_3^- and NO_2^- (up to ~70‰ and 50‰) ever reported to date in OMZs near the center of the eddy. N deficit and biogenic N_2-N concentrations were also the highest near the center of this eddy (up to ~40 µmol/kg), where $d^{15}N$-N_2 varied with biogenic N_2 production, following kinetic isotopic fractionation during NO_2^- reduction to N_2. We calculated variable isotope effects for NO_3^- reduction (up to ~30‰ in the presence of NO_2^-). However, the net N-loss fractionation factor is calculated to be only 10 to 14‰ when the effect of NO_2^- oxidation in the OMZ is removed using a closed system model that includes both the substrate (NO_3- and NO_2^-) and product (biogenic N_2) pools. Similarly, we calculated an isotope effect for NO_2^- reduction to N_2 of ~12‰ when NO_3^- was completely consumed. Our results confirm the role of NO_2^- oxidation in increasing the e effect associated with NO_3^- reduction in the ETSP and imply a lower net e associated with N-loss than the value of ~20-30‰ previously reported in marine environments, with important implications for the global marine N budget.

Changes in active mixing as a driver of subpolar phytoplankton blooms: An examination at large and small scales

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The timing of the spring phytoplankton bloom in subpolar regions has important consequences for marine ecosystems and carbon cycling. These blooms export large and variable amounts of carbon dioxide from the atmosphere to the deep ocean, and as such,

form an important component of the biological pump. The conventional explanation for the timing of subpolar phytoplankton blooms - that the shoaling of the seasonal mixed layer due to ocean surface warming reduces the depth to which phytoplankton are mixed, increases light availability, and prompts a bloom - has recently been challenged. Alternative hypotheses include the idea that decreases in turbulence, driven either by the onset of positive heat fluxes or by decreases in winds, prompt increased concentrations of phytoplankton at shallow depths in advance of the seasonal mixed layer shoaling, that stratification induced by mixed layer eddies drives the bloom prior to the onset of ocean surface warming, and that the deepening of the mixed layer in the winter reduces phytoplankton-grazer encounters and increases the integrated phytoplankton population. Because blooms that occur in unstratified waters have the potential to export more carbon that those that occur in stratified waters, these different theories have implications for the biological pump.

In this analysis, we use remotely sensed chlorophyll and atmospheric forcing data to examine these varying hypotheses for the timing of the subpolar phytoplankton bloom at the basin scale. We find that none of the recently proposed mechansims can fully explain the observed bloom timing. We then propose a model for bloom initiation based on decreases in the active mixing depth of the upper ocean, which we parameterize based on a combination of mixed layer depth, heat flux, and wind information. We hypothesize that the active mixing depth shoals as mixing in the upper ocean shifts from buoyancy-driven to wind-driven. We find that at the basin scale, decreases in the active mixing depth correlates strongly with the increased chlorophyll signal seen during the spring bloom. We further confirm our hypothesis by examining this theory with depth-integrated biomass and water column density data from the North Atlantic Bloom 2008 (NAB08) experiment. Again, we find a strong relationship between decreases in the active mixing depth and the onset of the bloom in the record. Finally, we use the NAB08 data to examine our hypothesis that upper ocean mixing shifts from buoyancy-driven to wind-driven prior to the bloom, and again find support for this hypothesis in the in situ record of mixing.

Automated imaging to examine ciliate communities

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Ciliates play important roles in grazing and nutrient recycling, but relatively little is known about their patterns of natural variability, due to difficulties in collecting, culturing, and observing these often-delicate cells. Imaging FlowCytobot (IFCB) helps to overcome observational challenges because it can be used to study live cells *in situ* without the need to culture or preserve during long-term deployments at the Martha's Vineyard Coastal Observatory. IFCB records images of cells with chlorophyll fluorescence above a trigger threshold, so to date analysis of the taxonomically-resolved time series of ciliates (2006-2014) has focused on mixotrophs and herbivores. Automated classification through the extraction of image features and a machine learning algorithm is used to evaluate these large high-resolution data sets; the results reveal varying seasonal patterns in abundance among groups of ciliates. To advance this observational technique, we have coupled a "live cell" fluorescent stain with a modified IFCB to allow imaging of a more complete community of ciliates (including those consuming bacteria and other heterotrophs). Preliminary field applications have revealed grazers not previously seen by IFCB, as well as increases in numbers observed for other groups.

Accurate oxygen from self-calibrating Argo floats in the North Pacific

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Annual net community production (ANCP) in the surface ocean is an important part of the marine carbon cycle and one of the primary controls on carbon dioxide levels in the atmosphere. Net biological oxygen production over the course of a year will be stoichiometrically related to ANCP. In order to calculate net biological production from oxygen measurements, accurate measurements are necessary to constrain the air-sea gas flux. Most oxygen measurements to date have been made from ship-based Winkler titrations, which can yield accurate data but are time intensive and limited in spatial and temporal resolution. In recent years, autonomous platforms such as floats and gliders have increasingly been used to provide high-temporal resolution oxygen data, but these data have largely been of uncertain accuracy and limited use.

This poster describes our efforts to calibrate Aanderaa oxygen sensors in-situ on specially designed Argo floats deployed at Ocean Station Papa, in June 2012, and in the Kuroshio Extension in February and March 2013. Prior to deployment, each sensor was calibrated (in the lab) across a range of temperatures and oxygen saturations and in fresh and salt water. Each float was deployed directly after a calibration cast and then revisited between 2 and 14 days later for a second calibration cast. The floats were modified to fully expose the oxygen sensors to atmospheric air upon surfacing. Atmospheric pO_2 can be calculated using pressure reanalysis data and measured temperature, allowing these air measurements to be used for on-going in-situ calibration.

The air calibrations compare well with ship-based Winkler measurements, providing support for using this technique to replace costly calibration casts from research vessels. Surface supersaturation data from these floats show good agreement with climatological oxygen data from the World Ocean Atlas. Through this work we hope to add an important step towards the development of a global system of high accuracy oxygen measurements that will help answer fundamental questions about ocean oxygen cycles and changes.

Constraints on observationally intractable aspects of the mesopelagic carbon cycle: Comparison of direct observations and results from multi-parameter sensitivity analyses

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Large uncertainties continue to surround many of the parameters that define the mesopelagic carbon cycle, either because the metabolic rates on which they are based are not amenable to direct measurement, or because traditional methods are inadequate to resolve them with sufficient resolution. Here, we pair observations at six stations in the North Atlantic Ocean with sensitivity analyses of two simple models to place constraints on several parameters associated with particle flux attenuation that have been traditionally difficult to measure. By comparing our model results to measurements of particulate carbon fluxes, bacterial production rates, and respiration by water column and particle-associated microbial communities, we obtain bounded estimates of bacterial growth efficiency (BGE), the average particle sinking velocity, and the fraction of bacterial production attributable to particle-attached communities (f_p). In addition, we use model-observed deviations to assess the relative importance in particle flux attenuation of respiration and dissolution/disaggregation. We estimated BGEs ranging from 0.05 at the subpolar site of a coccolithophore bloom, on large fluxes of sinking substrate high in PIC, to 0.40 at a temperate, mixed-community coastal site. Average particle sinking velocities ranged from 5 to 150 m d^{-1}. Over a range of reasonable sinking velocities for particles in the mesopelagic, disaggregation and dissolution were inconsequential as sinks for particle material relative to microbial respiration; only at very high modeled sinking velocities did comparison with observed fluxes allow for any significant disaggregation or dissolution. By contrast, the choice of BGE had a pronounced effect on modeled POC flux and, accordingly, deviation of model results from observed data.

A mechanistic particle flux model applied to the oceanic phosphorus cycle

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The sinking and decomposition of particulate organic matter are critical processes in the ocean's biological pump, but are poorly understood and crudely represented in biogeochemical models. Here we present a mechanistic model for particle fluxes in the

ocean that solves the evolution of the particle size distribution with depth. The model can represent a wide range of particle flux profiles, depending on the surface particle size distribution, the relationships between particle size, mass and velocity, and the rate of particle mass loss during decomposition. Spatially variable flux profiles are embedded in a data-constrained ocean circulation model, where the most uncertain parameters governing particle dynamics are tuned to achieve an optimal fit to the global distribution of phosphate. The resolution of spatially variable particle sizes has a significant effect on modeled organic matter production rates, increasing production in oligotrophic regions and decreasing production in eutrophic regions compared to a model that assumes spatially uniform particle sizes and sinking fluxes. The mechanistic particle model can reproduce global nutrient distributions better than, and sediment trap fluxes as well as, other commonly used empirical formulas. However, these independent data constraints cannot be simultaneously matched in a closed P budget commonly assumed in ocean models. Through a systematic addition of model processes, we show that the apparent discrepancy between particle flux and nutrient data can be resolved through P burial, but only if that burial is associated with a slowly decaying component of organic matter as might be achieved through protection by ballast minerals. Moreover, the model solution that best matches both datasets requires a larger rate of P burial (and compensating inputs) than have been previously estimated. Our results imply a marine PO_4 inventory with a residence time of a few thousand years, similar to that of the relatively dynamic N cycle.

The response of particle associated microbes to diatom derived oxylipins: A tale of enhanced nutrient recycling on sinking particles

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Many diatom species produce oxylipins, a diverse, bioactive class of compounds. Oxylipins produced by diatoms, particularly polyunsaturated aldehydes (PUAs), can impact the growth, survival, and reproductive success of organisms on various levels of the marine food web. In culture studies, PUA production increased when the cells were grown under nutrient limiting conditions or experienced grazing, both bloom termination mechanisms. During this study our objective was to determine how PUAs might affect the remineralization of diatom derived organic matter and subsequent recycling of nutrients. We conducted incubation experiments exposing sinking particles collected from 50m in the water column to varying concentrations of PUAs. This experiment was conducted three times. Sinking particles for Experiment 1 were collected from a declining bloom. Experiments 2 and 3 were set-up using sinking particles from nutrient replete, early-bloom conditions. In Experiment 1, the particle associated microbial

community exhibited alkaline phosphatase activities 5 to 8-times higher than the control when exposed to PUA concentrations of 10 and 100uM, respectively. Additionally in the 100uM treatments, the protease activity of the microbial community decreased slightly compared to the control yet the dissolution of bSi significantly increased. This is an intriguing result considering that the dissolution of bSi is typically associated with high protease activity. At stations O-2 and O-3, the dissolution of bSi remained constant over all PUA concentrations tested. APase activity double compared to the control when the community was exposed to 10uM PUA but signifcantly decreased at 100uM, demonstrating a much weaker stimulation compared to Experiment 1. Whereas, peptidase activity significantly decreased with increasing PUA concentrations. We hypothesize that enhanced oxylipin production during bloom decline may alleviate nutrient stress by increasing the dissolution of bSi and increasing the regeneration of inorganic phosphorus via APase activity. During early-bloom conditions, there may be some enhanced regeneration of inorganic phosphorus at intermediate concentrations of PUAs but the response is relatively weaker. Furthermore, the particle-associated microbial community from early-bloom conditions appeared to be suppressed by exposure to high concentrations of PUAs. This observation is consistent with recent work suggesting that PUAs may play a role in bacterial community succession on sinking particles.

Benefit of a patchy habitat for a kinesis-exhibiting particle population

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We use a simple two-dimensional, individual-based model to show that patchiness of a nutrient field enhances the foraging success of a kinesis-exhibiting population of particles in terms of nutrient uptake rates, encounter rates and energy efficiency.

Our definition of patchiness takes into account two parameters: the area of tracer compared to the area of no tracer and the slope of the tracer variance spectrum. We use this definition to introduce a certain patchiness of the nutrient field. Kinesis is then implemented by modifying a standard random walk model. Here the random walk length is made a function of the local nutrient concentration resulting in a slowing down of particles on favorable spots and speeding up on less favorable spots.

In an extension of the problem, we find that a randomly stirring velocity field, that advects both the particle population and the nutrient field, significantly modifies the relationship between patchiness of nutrients and foraging success. Major reason for that is that stirring breaks down patches of nutrients to smaller scales and enhances gradients. The overall effect is a decrease in foraging success.

A renovating wave model is used to simulate the random advection. The velocity field is prescribed at every time step and switched instantaneously to a new field after a fixed period of time. Both particles and nutrients are advected in a Lagrangian framework, in order to minimize numerical diffusion.

Distribution of transparent exopolymer particles across an organic carbon gradient from a North Atlantic bloom to the Sargasso Sea

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Transparent exopolymer particles (TEP) are macrogels that can reach millimeters in size and abiotically assemble from dissolved acidic polysaccharides. TEP formation is controlled by the composition and concentration of precursor material as well as physical aggregation processes. In this study, the abundance of TEP is examined across a TOC gradient from a phytoplankton bloom region in the North Atlantic to oligotropic waters in the Sargasso Sea. Four distinct regions with varying chlorophyll, temperature, and salinity are sampled in surface and column seawater as well as the overlying sea surface microlayer (SML). Similar to a previous study (Wurl et al., 2011), TEP concentration in the sea surface microlayer (SML) was enhanced relative to surface and column seawater and showed no correlation to chlorophyll concentration. The abiotic formation, recycling, degradation, and vertical transport of TEP are poorly understood processes involved in the partitioning and transformation of organic carbon in the surface ocean. More comprehensive analyses of TEP distributions with different seawater properties are required to accurately describe the role of TEP in the carbon cycle.

Non-Redfield DOM dynamics and preferential remineralization of dissolved organic phosphorus in the global ocean

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Marine geochemists have long used the Redfield ratio to link nutrient cycles of N and P to fixed C, allowing quantification of carbon export by applying a fixed ratio of C:N:P for organic matter over regional to global scales. Thus the Redfield ratio underlies assumptions regarding current estimates of the strength and resiliency of the biological pump to future perturbations. Dissolved organic matter (DOM) is an important pool within the biological pump, providing an advective pathway for removal of ~20% of export production. Here we compile observations of marine DOM to show deviations from Redfield stoichiometry within the DOM pool both across ocean basins and globally. Marine DOM is enriched in C and N compared to Redfield stoichiometry, averaging 286:36:1 and 809:48:1 for C:N:P within the degradable and total bulk pools, respectively. Dissolved organic phosphorus (DOP) is found to be preferentially remineralized with respect to both the Redfield ratio and the enriched C:N stoichiometry of marine DOM. Biogeochemical modeling with the CESM-BEC using Redfield and variable DOM cycling stoichiometry cases corroborate the need for non-Redfield dynamics to match the

observed DOM stoichiometry. From our model simulations, preferential DOP remineralization is found to increase the strength of the biological pump by ~9%, with largest increases in C export occurring along the western sides of the major ocean basins versus the case of Redfield DOM cycling. Global net primary productivity increases ~10% including an increase in marine nitrogen fixation of ~26% when preferential DOP remineralization is considered. The largest changes in marine nitrogen fixation are observed within the western subtropical gyres, suggesting the lateral transfer of P in the form of DOP from productive eastern gyre margins may be important for sustaining elevated nitrogen fixation rates downstream in the subtropical gyres.

Biogeochemistry of the deep Gulf of Mexico

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The biogeochemical components of seawater (carbon, oxygen, nutrients) from the Caribbean Sea and western North Atlantic were employed to characterize the water masses within the Gulf of Mexico. Gradients within the system have been assessed to infer inter-basin exchanges of water masses and the physical and biogeochemical processes occurring within the deep gulf.

Export production for the Western Antarctic Peninsula (WAP) region: Implications in a warming ocean

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The waters off the western Antarctic Peninsula (WAP) may be impacted significantly by recent global warming and climate change with potential impacts on export production (EP). Climatological means of EP for the WAP were computed to be 81.3 ± 47.9 and 8.2 ± 5.1 mg C m^{-2} d^{-1} for coastal (inshore) and mid-shelf (offshore) sub-regions, respectively with export ratios (e-ratios) ranging from 0.8 – 7.9%. These ratios are in close agreement with previous work from the region. A harmonic regression fit of EP against potential new production (PNP, a proxy for new production) gave a positive correlation (R^2 = 0.62,

N = 67) during the growth season (November – February). Depth adjusted ^{234}Th-derived EP ranged between 31 to 1101 mg C m^{-2} d^{-1} (Mean = 442 ± 289 mg C m^{-2} d^{-1}, N = 21). These estimates provided an e-ratio of 43%, an order of magnitude larger than those from sediment trap estimates. A striking characteristic of the WAP is the temporal and spatial variability of EP. Our analysis showed a negative correlation between EP and ice days and temperature. The WAP region demonstrated a large interannual variability of mean EP for those years analyzed (1992 – 2013) with a negative slope of 0.68 (R = -0.54, n = 20). This downward trend in mean EP implies that these waters could act less as a carbon sink even during the growth season signifying a decrease in carbon sequestration as a result of recent global warming.

Antioxidant activity (free radical scavenging) of dissolved organic matter

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Dissolved organic matter (DOM) serves a variety of critical biogeochemical functions in aquatic ecosystems. Among these its capacity as free radical scavenger has not been properly explored. DOM can act as electron donor and as such is expected to disrupt free radical chain reactions acting as an antioxidant. Here we describe a simple analytical method to assess the free radical scavenging capacity of the dissolved organic matter, and apply it to a set of samples featuring significant differences in DOM source (and composition) from Everglades National Park and Florida Bay. The free radical scavenging capacity was compared between samples from different environmental settings and along two salinity gradients from tidal fringe mangrove streams. All of the samples presented antioxidant activity in different quantities depending on their origin and thus DOM quality. Although linear correlations between DOC, CDOM and free radical scavenging activity were observed, carbon-normalized data showed clearly that samples associated with mangroves areas presented the highest free radical scavenging capacity possibly due to the presence of tannins which are known to be powerful antioxidants. The presence of antioxidants may have important implications in aquatic photochemistry as well as in the microbial activity.

Beyond minerals: Probing the mechanisms of particulate organic carbon transfer across the Great Calcite Belt

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Sequestration of carbon by the marine biological pump depends on the processes that alter, remineralize and preserve particulate organic carbon (POC) during transit to the deep ocean. Here, we present data collected from the Great Calcite Belt region of the Southern Ocean to compare the transformation of POC in the euphotic and mesopelagic zones of the water column. POC, particulate inorganic carbon (PIC), and biogenic silica (BSi) concentrations, and ^{234}Th-derived fluxes of each, were measured from two particle size-fractions collected within the upper 1000m of 27 stations across the Atlantic and Indian sectors of the Great Belt. POC export out of the euphotic zone was correlated with BSi export. PIC export was not, but was correlated with POC transfer efficiency in the mesopelagic zone. Regions of high [BSi] tended to have proportionally larger particles and high export efficiency, but also exhibited higher attenuation of [POC] in the mesopelagic zone. Further, particle size distribution was more strongly correlated to POC transfer through the mesopelagic zone than were mineral concentrations. We suggest that particle size reflects phytoplankton community composition across the Great Belt. In turn, the distinct recycling regimes associated with these communities control the sequestration potential of CO_2 fixed in the euphotic zone. For example, larger particles at BSi-rich diatom-dominated stations would be exported efficiently out of the euphotic zone but recycled vigorously down the mesopelagic, while the converse would occur in PIC-rich coccolithophore-dominated communities that produce smaller particles. Going forward, we hope to further explore the connection between primary producers and POC degradation using a suite of organic geochemical characterization techniques. These preliminary conclusions imply that phytoplankton responses to ocean warming and acidification could shift the sequestration potential of sinking particulate organic carbon.

EXport Processes in the Ocean from Remote Sensing (EXPORTS): Science plan for a NASA field campaign to quantify the biological pump using satellite observables

D. Siegel and EXPORTS Science Plan Writing Team

Assessment of the strength and efficiency of the ocean's biological carbon pump is important for understanding the roles of marine ecosystems on atmospheric CO2 levels and their feedbacks to the Earth's climate. However our capability to quantify present and predict future states of the biological pump are primitive at best. Here, we introduce plans for a NASA field campaign, EXport Processes in the Ocean from Remote Sensing (EXPORTS), to address the quantification of the state of the biological pump from satellite observables. New remote sensing and in situ observing technologies have been developed that extend our observational capabilities beyond bulk measurements of a few surface ocean properties. Coupling these new capabilities with numerical models will enable us to move from local to global predictive understanding of role of changing plankton ecosystems on the functioning of the biological pump. The EXPORTS science plan focuses on two sites, the N. Pacific (Station P) and N. Atlantic, using two process studies at each site to capture different states of the ocean's biological pump. The field work will include ships, floats, gliders and remote sensing analyses. Modeling will be required to plan the best sampling strategies, to assimilate observations and make predictive assessments of the response of the biological pump to key physical and biological processes. The development of the EXPORTS science plan has had extensive community vetting and the submitted science plan is presently under community review conducted by NASA (see http://cce.nasa.gov/cce/ocean_exports_intro.htm for more information).

Group behavior among model bacteria influences particulate carbon remineralization depths

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Organic particles sinking from the sunlit surface are oases of food for heterotrophic bacteria living in the deep ocean. Bacteria need to solubilize particles, so they produce exoenzymes, which cleave bonds to make molecules small enough to be transported through bacterial cell walls. Releasing exoenzymes, which have an energetic cost, to the external environment is risky because there is no guarantee that products of exoenzyme activity, called hydrolysate, will diffuse to the bacterium that produced the exoenzymes. Strategies used by bacteria to counteract diffusive losses of exoenzymes and hydrolysate are investigated in a water column model. We find that production of exoenzymes by particle-attached bacteria is only energetically worthwhile at high bacterial abundances. Quorum sensing provides the means to determine local abundances, and thus the model results support lab and field studies which found that particle-attached bacteria have the ability to use quorum sensing. Additional model results are that bacterial production is sensitive to diffusion of hydrolysate from the particle and is enhanced by as much as 15× when diffusion of exoenzymes and hydrolysate from particles is reduced by barriers of bacteria. Bacterial colonization rates and activities on particles in both the euphotic and mesopelagic zones impact remineralization length scales. Shoaling or deepening of the remineralization depth has been shown to exert significant influence on the residence time and concentration of carbon in the atmosphere and ocean. By linking variability in remineralization depths to mechanisms governing bacterial colonization of particles and group coordination of exoenzyme production using a model, we quantitatively connect microscale bacteria-particle interactions to the carbon cycle and provide new insights for future observations.

The carbon flush – an inductive model explaining variability in copepod fecal pellet flux

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Zooplankton fecal pellet flux is a highly variable component of the biological carbon pump. While fecal pellets can comprise 0 to nearly 100% of particulate organic carbon collected in sediment traps, mechanisms for this variability remain poorly understood. We propose that total fecal pellet carbon production by a zooplankton community is not a sufficient estimate of flux, but rather, that flux depends primarily on zooplankton community size structure and secondarily on zooplankton abundance. We test this hypothesis by building a model of copepod fecal pellet carbon flux and applying it to twelve years of the Gulf of Maine Continuous Plankton Recorder copepod abundance time series. The model incorporates individual-scale metabolic processes, the influence of temperature on copepod body size, and a function representing the breakdown of particles in the water column. When applied to the copepod communities sampled in the Gulf of Maine, a seasonal pattern of fecal pellet carbon flux emerges that is similar to patterns seen in Gulf of Maine sediment traps. The interannual flux time series produced by the model mirrors growth of a Gulf of Maine quahog, suggesting that a size-structured analysis can also explain changes in carbon availability to the benthos. We conclude that fecal pellet carbon flux in the Gulf of Maine is driven primarily by copepod community size structure, rather than copepod abundance alone, and that changes in the physical environment that alter the composition of the copepod community lead to variability in fecal pellet carbon flux.

Global-scale variations in the carbon to phosphorous ratio of exported marine organic matter

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The carbon-to-phosphorus (C:P) ratios of organic matter production and export are fundamental to linking marine ecosystems to the Earth's carbon cycle. A recent analysis of the C:P ratio in surface ocean phytoplankton has revealed variations with strong latitudinal patterns (Martiny et al. 2013). A question of great importance for the ocean's carbon pump is how much of this spatial variability is exported with the organic matter that remineralizes in the thermocline and deeper waters. We address this question by estimating the C:P ratio of exported organic matter using a biogeochemical inverse model based on a recently developed data-constrained ocean circulation model and a global database of hydrographic DIC and PO_4 measurements (Key et al. 2004; Garcia et al. 2010; Primeau et al. 2013). Our analysis reveals for the first time the global patterns of variability in the carbon-to-phosphorus ratio of exported organic matter, $(C:P)_{exp}$. We find elevated $(C:P)_{exp}$ values in the nutrient-depleted subtropical gyres (carbon-export weighted average of 178) and depressed $(C:P)_{exp}$ values in nutrient-rich upwelling and high latitude regions (carbon-export weighted average of 87). We also find substantial differences between the gyres. Carbon export inferred from our model with regionally distinct $(C:P)_{exp}$ is much less regionally variable than with constant Redfield

stoichiometry and in better agreement with available experimentally determined estimates of annual net community production (Emerson 2014). Overall, the inferred patterns of C:P variability for exported organic matter are consistent with the large-scale elemental stoichiometry variations in available phytoplankton and suspended particulate matter measurements. This result supports the hypothesis that planktonic C:P variability contributes to C:P variability in the remineralization flux at depth.

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Air-sea exchange of CO_2 in the East China Sea: Synthesis, time-series and mechanisms

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Limited observations exist for reliable assessment of unusually large CO_2 uptake with temporal variability and controlling mechanisms in the river-dominated East China Sea (ECS). Here we show evidence of strong control of river runoff on the CO_2 uptake capacity of the ECS. From observations over a 14-year period in the productive ECS shelf, we firstly identified the biological sequestration of CO_2 taking place in the highly productive Changjiang river plume in warm seasons due to riverine nutrient enrichment. Accordingly, changes in the plume area due to changes in Changjiang discharge strongly affect the CO_2 uptake capacity. Further, we have established an empirical algorithm as a function of sea surface temperature (SST) and Changjiang river discharge (CRD) for predicting sea surface pCO_2. Synthesis based on both observation and model show that the annually averaged CO_2 uptake from atmosphere during 1998-2011 was constrained to about 1.8±0.5 mol C m^{-2} y^{-1}. This assessment of annual CO_2 uptake is more reliable and representative, compared to previous estimates, in terms of temporal and spatial coverage. Additionally, the CO_2 time-series, exhibiting distinct seasonal pattern, gives mean fluxes of -3.7±0.5, -1.1±1.3, -0.3±0.8 and -2.5±0.7 mol C m^{-2} y^{-1} in spring, summer, fall and winter, respectively, and also reveals apparent inter-annual variations. The flux seasonality shows a strong sink in spring and a weak source in late summer - mid-fall. The weak sink status during warm periods in summer-fall is fairly sensitive to changes of pCO_2 and may easily shift from a sink to a source altered by environmental changes under climate change and anthropogenic forcing, e.g., the operation of Three Gorges Dam and water transferring scheme from the south to north in China, decreasing the Changjiang river discharge and then resulting in reduction in CO_2 uptake capacity.

Evaluating particle abundances and chlorophyll *a* concentrations in the northern coastal Gulf of Alaska

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The northern coastal Gulf of Alaska (GOA) is part of a long term observational program to collect basic physical, chemical, and biological data each spring and fall. However, this region lacks a recent analysis of the behavior of particulate organic matter. This study seeks to analyze particle abundances and size distributions over the northern GOA shelf. Profiles were collected in May 2014 on the first of four cruises along the Seward Line in the coastal GOA, using the Underwater Vision Profiler (UVP) to take *in situ* optical images. The UVP provides a high-resolution dataset of particle abundances and size distributions, and images are sorted by particle type using Zooprocess software. This will allow for exploration of the spatial and temporal variability in particulate organic matter, in order to evaluate the relationships between particle abundances, chlorophyll *a* concentrations, and macronutrient concentrations. In May 2014, overall particle abundances decreased with distance from shore, with subsurface maxima and some weak resemblance to the spatial patterns of chlorophyll *a* concentrations. Future data collection and temporal comparisons will help us investigate the relationships between the timing and magnitude of primary production and sinking particle flux in this high-latitude system.

Using likelihood method and total inverse method towards the MedFlux sediment trap data to investigate particle cycling in the ocean

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Abstract: the maximum likelihood method and total inverse method together have been applied to MedFlux settling velocity (SV) sediment trap data, which include particle settling velocity, particle mass and thorium isotope (^{234}Th and ^{230}Th) activities in each settling velocity class. The conceptual model of Szlosek et al. (2009) was formularized by assuming steady state and first-order reaction kinetics for thorium adsorption and desorption, and for particle aggregation and disaggregation. The maximum likelihood method indicates that particles with a settling velocity of 11 m/d and above should be treated as the fast sinking category in the conceptual model in Szlosek et al. (2009), and the remaining SV classes as the slowly sinking category. The total inverse method shows the adsorption rate constants for both slowly and fast sinking particles increase slightly with depth. The desorption rate constants increase with depth from 0.76 to 3.43 y^{-1} for slowly settling particles, from 3.03 to 6.75 y^{-1} for fast settling particles. The aggregation rate and disaggregation rate constants remain nearly constant throughout the transition from shallow (~300 m) to deep (~1900 m) trap depths. Production from ^{238}U decay is the

main source of Th; radioactive decay and adsorption by particles are the main sink for dissolved ^{234}Th. For rapidly sinking particles, adsorption is the main source; radioactive decay and flux-out are the main sink. For slowly sinking particles, adsorption is the main source; radioactive decay and desorption are the main sinks. For particulate ^{230}Th, the contributions from aggregation and disaggregation become more important.

Spatial and temporal flux variability of diatom species, biogenic silica, and particulate organic carbon in the Gulf of Maine

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The highly productive Gulf of Maine shelf system is generally divided into eastern and western regions based on hydrography and major current flow patterns. Eastern gulf regions exhibit weaker stratification, stronger tidal flows, periodic upwelling, and higher nutrient levels than the more strongly stratified western gulf. It is hypothesized that diatom fluxes will vary between the east and west as a result of these water column characteristics. While it has been shown that variations exist between western and eastern gulf regions in terms of the mass flux of organic carbon and biogenic opal, the seasonal flux and deep-water delivery of diatoms within these regions has not been examined. In the present study, high resolution, time-series sediment traps were deployed for 8-12 months in Wilkinson and Jordan Basins (representing the western and eastern gulf, respectively) in order to quantify the inter-annual variation of numerical and species fluxes of diatoms, as well as the simultaneous particulate organic carbon (POC) and opal mass fluxes. Strong seasonal signals were observed in total diatom fluxes and species abundance based on trap collections at 95-150 m, with distinct inter-basinal differences. Jordan Basin (eastern gulf) displayed greater diatom fluxes than Wilkinson Basin (western gulf) during spring and fall blooms. The greatest flux was $3.2x10^7 frustules \cdot m^{-2} \cdot day^{-1}$ during the fall bloom in the eastern gulf (compared to a peak flux of $6.6x10^6 frustules \cdot m^{-2} \cdot day^{-1}$ in the western gulf). In both regions, T*halassionema nitzschioides* was found to be a common species throughout all trap-collected, sinking particulate samples, however, each region showed distinct differences in the species' abundance over time: *T. nitzschioides* fluctuated from <10% to >50% of the total diatom abundance in the western gulf, whereas in the eastern gulf it was consistently the most abundant diatom species (comprising >25% of its diatom flux). These findings are supported by the POC and biogenic opal mass fluxes, and their implications for the underlying recent sedimentary record of diatom production and delivery to the basins are presented.

Modeling pCO$_2$ variability in the Gulf of Mexico

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A three-dimensional coupled physical-biogeochemical model was used to simulate and examine temporal and spatial variability of surface pCO_2 in the Gulf of Mexico (GoM). The model is driven by realistic atmospheric forcing, open boundary conditions from a data-assimilative global ocean circulation model, and observed freshwater and terrestrial nutrient and carbon input from major rivers. A seven-year model hindcast (2004–2010) was performed and was validated against in situ measurements. The model revealed clear seasonality in surface pCO_2. The air-sea flux is estimated based on the multi-year mean of the model results. Overall, the GoM is a CO_2 sink with a flux of 1.34×10^{12} mol C yr^{-1}, which, together with the enormous fluvial carbon input, is balanced by the carbon export through the Loop Current. In addition, a sensitivity experiment was performed where all biological sources and sinks of carbon were disabled. In this simulation surface pCO_2 is elevated by ~70 ppm, suggesting that biological uptake is the most important reason for the observed CO_2 sink. Factors controlling the spatial distribution of surface pCO_2 and uncertainties in the carbon budget estimation are also discussed.

Exploring a microbial ecosystem approach to modeling deep ocean biogeochemical cycles

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Though microbial respiration of organic matter in the deep ocean governs ocean and atmosphere biogeochemistry, it is not represented mechanistically in current global biogeochemical models. We seek approaches that are feasible for a global resolution, yet still reflect the enormous biodiversity of the deep microbial community and its associated metabolic pathways. We present a modeling framework grounded in thermodynamics and redox reaction stoichiometry that represents diverse microbial metabolisms explicitly. We describe a bacterial/archaeal functional type with two parameters: a growth efficiency representing the chemistry underlying a bacterial metabolism, and a rate limitation given by the rate of uptake of each of the necessary substrates for that metabolism. We then apply this approach to answer questions about microbial ecology. As a start, we resolve two dominant heterotrophic respiratory pathways- reduction of oxygen and nitrate- and associated microbial functional types. We combine these into an ecological model and a two-dimensional ocean circulation model to explore the organization, biogeochemistry, and ecology of oxygen minimum zones. Intensified upwelling and lateral transport conspire to produce an oxygen minimum at mid-depth,

populated by anaerobic denitrifiers. This modeling approach should ultimately allow for the emergence of bacterial biogeography from competition of metabolisms and for the incorporation of microbial feedbacks to the climate system.

Advances in our Understanding of the Role of Sea Ice in the Global Carbon Cycle (Wednesday, 7/23)

Biogeochemical modifications of water masses on the Ross Sea shelf

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The shelf systems of Antarctica play important roles in the modification of major water masses, primarily in the formation of Antarctic Bottom Water. One such system is the Ross Sea, which lies on a biologically productive shelf where water mass modification is seasonal and tied to extensive polynyas. Though the hydrography of the Ross Sea has been well researched, as it is key to global ocean overturning circulation, the biogeochemical modifications of its water masses have not been carefully studied. It is important to understand the biogeochemical fate of these water masses due to the substantial impacts of changing climate on polar shelf ecosystems. Some of these impacts, such as freshening of shelf waters due to increased precipitation and ice melt, have already been observed in the Ross Sea.

In this study, we use data obtained from oceanographic expeditions in the Ross Sea (NBP 1302) and Southern Ocean (CLIVAR S4P). The biogeochemical components of interest from these data include dissolved oxygen, carbon, and nutrients, introduced into the system via their fluxes associated with the biological pump (the main force behind sequestration of carbon from the atmosphere to the deep ocean). Using these data paired with hydrological data, we investigate and quantify the transformations of biogeochemical components of the water masses found in the Ross Sea and determine whether these modifications are seen in Antarctic Bottom Water formation at the continental shelf break.

Parameterizing bubble-mediated air-sea gas exchange and its effect on ocean ventilation

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Bubbles play an important role in the exchange of gases between the atmosphere and ocean, altering both the rate of exchange and the equilibrium gas saturation state. We develop a parameterization of bubble-mediated gas fluxes for use in Earth system models. The parameterization is derived from a mechanistic model of the oceanic boundary layer that simulates turbulent flows and the size spectrum of bubbles across a range of wind speeds and is compared against other published formulations. Bubble-induced surface supersaturation increases rapidly with wind speed and is inversely related to temperature at a given wind speed, making the effect of bubbles greatest in regions that ventilate the deep ocean. The bubble-induced supersaturation in high-latitude surface waters compensates a substantial fraction of the undersaturation caused by surface cooling. Using a global ocean transport model, we show that this parameterization reproduces observed saturation rate profiles of the noble gas Argon in the deep Atlantic and Pacific Oceans. The abyssal argon supersaturation caused by bubbles varies according to gas solubility, ranging from ~0.7% for soluble gases like CO_2 to ~1.7% for less soluble gases such as N_2. Bubble-induced supersaturation may be significant for biologically active gases such as oxygen.

Quantifying biological production during seasonal ice melt in the Bras d'Or Lakes, an inland sea in Nova Scotia, Canada

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In polar regions, sea ice regulates the annual cycle of biological activity. Ice cover in the Arctic has decreased over the past three decades, perturbing the Arctic carbon cycle. There are large uncertainties in the future effects of climate change on Arctic carbon fluxes. Very few in situ measurements of productivity during ice melt in saline waters have been published. Additionally, recent publications have reported conflicting results on the most accurate way to parameterize gas fluxes in partially ice-covered waters.

In order to investigate the effect of ice melt on productivity and air-sea gas exchange, we conducted a monthlong field campaign in the Bras d'Or Lakes, Nova Scotia, Canada during spring 2013. The Bras d'Or Lakes are a brackish inland sea with seasonal ice cover, and we collected data in Whycocomagh Bay, a basin within the sea, as it transitioned from fully ice covered to ice free. We set up a mooring to continuously pump water to shore and measured O_2/Ar gas ratios continuously and the triple oxygen isotope composition of O_2 discretely. These measurements enable determination of both gross primary and net community productivity. Dual tracer ($^3He/SF_6$) release experiments were conducted at varying levels of ice cover and will be used to parameterize air-sea gas

exchange throughout the experiment. In this poster, a preliminary analysis of the triple oxygen isotope and O_2/Ar data will be presented.

Modeling the impacts of organic macromolecules and chlorophyll on Arctic sea ice

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High amounts of organic macromolecules and chlorophyll are produced in global sea ice by the bottom community and also in vertically distributed layers where substantial biological activities take place. Brine channeling in columnar ice can allow for upward flow of nutrients, which leads to greater primary production in the presence of moderate light. Modeling of the situation can complement both experimental work and observations in the field. The project described here extends our study on the fluxes of organic macromolecules in the global ocean. We are now designing and conducting global climate model experiments to determine the impact of organic macromolecules and chlorophyll on Arctic sea ice. Influences on brine network permeability and radiation/albedo will be considered in this exercise. In addition to soot deposition on the ice and snow pack, ice algal chlorophyll is likely to compete as an absorber and redistributor of energy. Absorption by anthropogenic materials such as soot and black carbon will be compared with that of natural pigments. We will map areas of soot versus biological absorption dominance in the sense of single scattering, then couple into a full radiation transfer scheme to attribute the various contributions to polar climate change amplification. The work prepares us to study more traditional issues such as chlorophyll warming of the pack periphery and chemical effects of the flow of organics from ice internal communities. The experiments will begin in the Arctic but later we will broaden to include Antarctic sea ice and shelves.

The role of sea ice in regulating potential ecosystem export efficiency on the Eastern Bering Sea shelf – implications for benthic vs. pelagic ecosystem proliferation

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Spring and summer rates of Net Community and Gross Photosynthetic Production (NCP and GPP) were determined on seasonally ice-covered Eastern Bering Sea shelf from the simultaneous measurements of O_2/Ar and Triple Oxygen Isotope composition of dissolved O_2. NCP rates were converted from biological O_2 fluxes, or Net Oxygen

Production (NOP), using a photosynthetic O_2/C quotient. NCP/GPP ratios were used as a measure of potential ecosystem export efficiency.

Summer NCP, integrated over the June-September period, was estimated as 3.6±1.2 mol-Cm^{-2}. NCP of similar magnitude, 3.3±1.2 mol-Cm^{-2}, but over 4 times shorter time period was constrained for the spring bloom production within the Marginal Ice Zone (MIZ) in late April-May. Strong seasonal variability was observed in daily NCP, GPP and instantaneous NCP/GPP ratios. Within the MIZ spring blooms, daily NCP fluxes increased from ≤1 to >600 mmol-$Cm^{-2}d^{-1}$ through the progression of the bloom, with an average value of 110±40 mmol-$Cm^{-2}d^{-1}$. Summer NCP rates averaged 30±11 mmol-$Cm^{-2}d^{-1}$. Instantaneous daily NCP/GPP ratios in the MIZ blooms were 0.32 ±0.07 (n=23), exceeding by a factor of 3 the average summer ratios of 0.12 ± 0.02 (n=31). Maximum NCP/GPP ratios of 0.45 ± 0.07 (equivalent NOP/GPP ratios of 0.63) were observed within the mixed layers of 15-20 m. Statistically significant correlation between the NCP/GPP ratios and mixed layer depth, as well as water column stratification, was documented in spring, but not in summer, identifying water column stabilization by the melting ice as one of the drivers of the exceptionally high export efficiency of the spring blooms. The high values of NCP/GPP observed on the Bering Sea shelf reach a likely upper limit of the phytoplankton carbon fixation efficiency on the physiological level, and suggest very small contribution of the heterotrophic recycling at the time of the MIZ blooms on the ecosystem level. Similarly high NOP/GPP ratios were recently reported from the Southern Ocean by (Goldman et al. in review, Kranz et al., in review), who demonstrated the role of low temperatures growth in the efficiency of photosynthetic carbon fixation. In contrast to low latitude oceans, where stratified water column reduces nutrient transport to the euphotic zone, in seasonally ice covered seas, stabilization of the water column by melting ice under post-winter nutrient replete conditions is likely to promote an intense "pulse" of carbon export. Furthermore, high rate of plankton growth within shallow mixed layer may enhance sinking carbon flux by biomass aggregation (Jackson, 2008), thus likely increasing carbon delivery to benthic (vs. pelagic) ecosystem. Our findings highlight the role of sea-ice in regulating the pathways of carbon flow and the extent of the benthic-pelagic ecosystem coupling on the seasonally ice-covered shelf.

Sea ice flow patterns and ice edge blooms in the eastern Bering Sea

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Extraordinarily dense phytoplankton blooms may form in the Marginal Ice Zone (MIZ). These blooms dominate regional primary and export production and significantly influence later seasonal productivity by removing surface nutrients. While surface stability and phytoplankton seed stocks from the melting ice contribute to this important polar biological phenomenon, the flow patterns of the ice also play an important role in determining the location and intensity of the bloom. A coupled, atmosphere – ice –

ocean model was used to predict ice movement in the eastern Bering Sea during a 4-year field program. The largely wind-driven ice flow was critical in the year-to-year variations in ice edge blooms. The most intense blooms were associated with northerly winds that pushed coastal ice into warmer water in the outer shelf. We suspect that this flow pattern supplied trace metals from shallow polynyas to the melt zone that enhances productivity.

Future scenarios in the Ross Sea: Climate change impacts on circulation, water mass formation and biological responses

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The Ross Sea is presently undergoing rapid change, with increasing ice cover, reduced duration of ice-free periods, and significant freshening. However, global climate models predict that these recent changes in ice cover will soon reverse due to the increased atmospheric temperatures that are expected to develop. We present results of simulations of the oceanography of the Ross Sea in future years that may occur as a result of changes in atmospheric forcing (temperatures and winds), and speculate on the possible biological impacts of such changes. Changes that are predicted are altered date of opening and closing of the Ross Sea Polynya; increased ice-free duration; reduced ice cover in summer; shallower mixed layers in spring, summer and autumn; reduced, albeit only slightly, inputs of Modified Circumpolar Deep Water (MCDW); greatly reduced formation of dense High Salinity Shelf Water (HSSW); and slightly enhanced melting of the Ross Ice Shelf. All of these lead to increased productivity but with the loss of ice-dependent species, which likely will greatly modify the food web and biogeochemical cycles of the Ross Sea.

Impact of sea ice on the marine iron cycle and phytoplankton productivity

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Iron is a key nutrient for phytoplankton growth in the surface ocean. At high latitudes, the iron cycle is closely related to the dynamics of sea ice. In recent decades, Arctic sea ice cover has been declining rapidly and Antarctic sea ice has exhibited large regional trends. A significant reduction of sea ice in both hemispheres is projected in future climate scenarios. To study impacts of sea ice on the iron cycle, iron sequestration in ice has been incorporated into the Community Earth System Model (CESM). Sea ice acts as a reservoir for iron during winter and releases the trace metal to the surface ocean in spring and summer. Simulated iron concentrations in sea ice generally agree with observations,

in regions where iron concentrations are relatively low. The maximum iron concentrations simulated in Arctic and Antarctic sea ice are 192 nM and 134 nM respectively. These values are much lower than observed, which is likely due to underestimation of iron inputs to sea ice or missing mechanisms. The largest iron source to sea ice is suspended sediments, contributing fluxes of iron of 2.2×10^8 mol Fe/month in the Arctic and 4.1×10^6 mol Fe/month in the Southern Ocean during summer. As a result of the iron flux from ice, iron concentrations increase significantly in the Arctic. Iron released from melting ice increases phytoplankton production in spring and summer and shifts phytoplankton community composition in the Southern Ocean. Results for the period of 1998 to 2007 indicate that a reduction of sea ice in the Southern Ocean will have a negative influence on phytoplankton production.

Effects of ice floes and leads on air-sea gas transfer

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Seasonal ice zones (SIZ) play a central role in setting the air-sea CO_2 balance making them a critical component of the global carbon cycle. Incomplete understanding of how the sea-ice modulates gas fluxes renders it difficult to estimate the carbon budget in SIZ. Here, we investigate the turbulent mechanisms driving gas exchange in leads, polynyas and in the presence of ice floes.

The Gas Transfer through Polar Sea Ice experiment was performed at the US Army Cold Regions Research and Engineering Laboratory (Hanover, NH) under varying ice coverage, winds speed, fetch and currents. Supporting measurements were made of air and water temperature, humidity, salinity and wave height. Air-side profiling provided momentum, heat, and CO2 fluxes. Transfer velocities are also estimated via the active controlled flux technique. Surface turbulence statistics derived from PIV and optical flow applied to infrared imagery are linked to subsurface turbulence and used to investigate how turbulent mechanisms at the ice-water boundary including shear and buoyancy contribute to the magnitude of the transfer. Gas exchange variability with lead size and enhancement near floes will be examined.

Our results show that mixing is stronger at shorter fetch. Similarly, the gas transfer velocity, k, is stronger at shorter fetch and increases with wind speed. Variability due to currents is shown without a strong dependence on k in either lead.

For ice floes up to 37% coverage, mixing increases with ice floe coverage and is slightly dependent on pump speed and wind speed. Likewise, k increase with wind speed and k increases with ice floe concentrations increase from 13% to 37%. Variability accounts for pump speed variations that show slight increase in k with pump speed. The data suggests additional turbulence due to increased floe concentration enhances gas transfer. We hypothesize that k first increases with floe concentration, reaches a tipping point where concentration starts inhibiting turbulence and transfer.

General Interest (Wednesday, 7/23)

Emergent microbial metagenomes and metatranscriptomes in a model ocean

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To utilize new genomic understanding of marine microbes, we developed an ecosystem model whose community is determined by generating DNA for thousands of organisms through random assignment of functional genes. Microbes are assigned a size that sets their baseline environmental responses using allometry. These are modified by the ensemble of costs and benefits conferred by each gene in the organism's DNA. The model generates an emergent community and biogeochemistry similar to observed particle size and nutrient observations. Modeled gene transcription matches patterns observed recently along the extreme spatial gradient of the Amazon River plume. Based on a self-consistent ensemble of gene costs and benefits, the model predicts broad spatial patterns of gene abundance and expression that can be tested observationally, just as the cost-benefit patterns can be tested experimentally. The model explicitly links genomics and biogeochemistry and may be useful for determining impacts of climate change in the anthropocene.

Impacts of natural and anthropogenic climate variability on the Gulf of Mexico

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According to Liu et al. [2012], the surface temperature (SST) of the GoM may increase more than 1.5oC by the end of the 21st century. The observed SST in the GoM during the 20th century shows long-term SST variability similar to the Atlantic Multidecadal Oscillation. The amplitude of this multi-decadal signal is as large as 0.5oC, which is

comparable to the AGW-induced SST increase in the GoM by 2030. This means that the global warming-induced SST increase in the GoM can be doubled or nearly canceled out due to natural variability until the mid-21st century. Therefore, to further explore the impact of natural climate variability on the forced response of the GoM, here we perform dynamic downscaling of the surface-forced global ocean model simulation to the GoM region for the period of 1871-2008. The GFDL Modular Ocean Model, with the fully eddy-resolving horizontal resolution of about 10km in the GoM, is used as the downscaling model. The potential implications of natural and forced changes in the GoM on pelagic fish species and their spawning patterns are discussed.

The Amazon River Plume, diatom-diazotroph assemblages, and biogeochemistry of the tropical Atlantic

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The Amazon River delivers 1.93×10^5 m^3 of freshwater to the tropical Atlantic every second, forming a plume that can cover 1.2×10^6 km^2. The riverine nitrate is rapidly drawn down by coastal diatom blooms, but the Si and P exist at greater than Redfield ratios and hence persist after nitrate depletion, creating an ideal habitat space for nitrogen fixers, particularly diatom-diazotroph assemblages (DDA). To understand phytoplankton succession along the river-ocean gradient and determine the biogeochemical impact of this unique community, we constructed a 5-phytoplankton, 2-zooplankton ecological model and embedded it within a 1/6th degree HYCOM model of the tropical and subtropical Atlantic. By releasing synthetic Lagrangian floats in the model we were able to trace DDA bloom formation and found that bloom formation was stimulated by a decrease in grazing pressure and terminated by Si exhaustion. Bloom formation, however, also depended critically on reduced physical mixing that determined the duration that a water parcel spent in ideal bloom-formation conditions. N_2 fixation in the plume region (stimulated largely by DDA) was responsible for roughly half of total new production in the region. However, carbon export below the plume was significantly less than new production as much of the carbon (and nitrogen) fixed by the DDA was advected into the oligotrophic regions. The effect of the river on regions as distant as the Sargasso Sea was evident in climate scenarios showing that altered river discharge could significantly affect far field nitrogen fixation.