Eukaryotic metatranscriptomics illuminates physiological response of phytoplankton to nutrient pulses at Station ALOHA

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The reciprocal relationship between phytoplankton and their biogeochemical environment is central to our understanding of the marine carbon cycle. In many regards, however, we lack a fundamental understanding of how nutrients (particularly the macronutrients nitrogen, N, and phosphorus, P) are metabolized by different phytoplankton species: processes that may directly dictate their activities and, consequently, the impact on their biogeochemical environment. Novel metatranscriptomic techniques enable the \textit{in situ} observation of eukaryotic phytoplankton metabolic physiology in a species-specific fashion—a level of detail that is lost with most other bulk community assays. The hypothesized annual ‘summer export pulse’ (SEP), thought to represent an average of carbon export of 408 \( \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{d}^{-1} \), is likely correlated with a phytoplankton bloom event. Employing these new tools we sought to examine the effect of nutrient amendment on the phytoplankton community structure and physiology at Station ALOHA during the summer season. Two microcosm-scale 7-day incubations were performed in August of 2012 at Station ALOHA. Whole water incubations were conducted both with deep-water (10\% 700m water by volume) and with nutrient amendments modeled after this simulated deep-water mixing event. Nutrient-amended incubations were designed to drive the phytoplankton population towards nutrient limitation through the addition of everything except for nitrogen (-N) or phosphorus (-P) and towards nutrient repletion through the addition of the single nutrient N or P. The addition of deep water produced an increase in chlorophyll \( a \) concentration in both experiment 1 and 2 at the final time point (12.09 ± 0.85 and 7.81 ± 0.56 fold increase relative to the initial time points, respectively) and was similar to the changes in the –P treatment (10.36 ± 0.62 and 7.79 ± 0.34). Alkaline phosphatase activity (APA) assays were run on the second experiment, showing increased APA in both the deep water and –
P condition at the final time point. These data suggest that deep-water upwelling may drive the community towards P-limitation; a hypothesis that will be further investigated using the metatranscriptomic datasets, which will illuminate both shifts in the community composition and patterns of gene expression. Metatranscriptome samples were sequenced to 60 million 100 base-pair, paired end reads from the initial sample and each incubation. Current work is geared toward the development of a novel analysis pipeline for metatranscriptomic datasets to enable the identification of the species-specific nutrient niche partitioning strategies used within the phytoplankton community and provide new insights into the roles and activities of phytoplankton at Station ALOHA.

Biomass and primary productivity of picophytoplankton communities in warm-core and cold-core eddies in the Sargasso Sea

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The Sargasso Sea phytoplankton community is often dominated by picophytoplankton (0.7-2 microns). Mesoscale eddies, characterized by downwelling (warm-core) or upwelling (cold-core) circulations, are common physical features in the Sargasso Sea that alter physical, chemical, and biological characteristics of the surface ocean and thus impact resident phytoplankton and their rates of primary productivity. As part of the broader “Trophic BATS” project, we asked the question: Are there differences in the absolute and relative contributions of the picophytoplankton community to biomass and productivity between eddies of differing circulation? Experiments were conducted during four, two-week cruises in early spring (Feb-March) and summer (July-August) 2011 and 2012 within and outside of warm and cold core eddies. Picophytoplankton were the greatest contributors to euphotic-zone integrated chl a biomass (32-86% of total) and integrated productivity (56-93%) relative to larger phytoplankton at all stations. In 2011 integrated picophytoplankton biomass and rates of primary productivity were lower (as expected) in the spring warm-core eddy (7.7 mg chl a m⁻² and 52.2 mg C m⁻² d⁻¹) compared with outside (21.4 mg chl a m⁻² and 122.8 mg C m⁻² d⁻¹); in the summer cold-core eddy while biomass was lower in the eddy productivity was 18% higher relative to outside conditions. In 2012 both biomass and productivity were greater in the spring cold-core eddy but unexpectedly, were also greater in the summer warm-core eddy than outside. With the exception of the 2011 warm-core eddy, picophytoplankton productivity was 4-18% greater within eddies (compared to outside), and was (surprisingly) 14% higher in the warm-core eddy in summer 2012 than in both the cold-core eddies of 2011 and 2012.
Mesoscale eddies as fixed N-loss hotspots in the oxygen minimum zone off Peru

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Bioavailable fixed nitrogen (N) is well known as an essential macronutrient for phytoplankton that limits marine primary productivity throughout much of the ocean. The ocean’s fixed N inventory is controlled by the balance between sources and sinks. A large portion of the ocean’s fixed (i.e. bioavailable) N loss to N\textsubscript{2} gas takes place in Oxygen Minimum Zones (OMZs) even though they represent only 0.1% of the total oceanic volume. The responsible microbial processes are those favored under low O\textsubscript{2} conditions; denitrification and anammox. The causes of temporal and spatial variations in fixed N loss processes are not well understood, despite recent observations that suggest an intensification of the world’s OMZs in the future.

We present here clear evidence for mesoscale eddies as fixed N loss hotspots in OMZs. As such, they represent ‘natural experiments’ for understanding the large-scale processes controlling N-loss and the generation of corresponding biogeochemical signals. They also may be important for controlling the overall rate of N-loss in OMZ’s and their impact on the ocean’s N isotope budget. We observed 3 eddies in the Peru OMZ, 2 anticyclonic and 1 cyclonic as confirmed by sea level anomalies, sea surface temperatures, and chlorophyll\textsubscript{a} measurements, during two Meteor cruises in November and December 2012 (M90 and M91). In addition to standard hydrographic and nutrient properties, we measured the isotopic compositions of NO\textsubscript{3}\textsuperscript{-} and NO\textsubscript{2}\textsuperscript{-}, biogenic N\textsubscript{2} concentrations (from high precision N\textsubscript{2}/Ar measurements), and $\delta^{15}$N-N\textsubscript{2}.

The presence of N loss hotspots were confirmed by these biogeochemical parameters in the centers and edges of the eddies. Corresponding to the near exhaustion of NO\textsubscript{3}\textsuperscript{-}, we measured the highest d\textsuperscript{15}N values for both NO\textsubscript{2}\textsuperscript{-} and NO\textsubscript{3}\textsuperscript{-} (up to $\sim$50‰ and $\sim$70‰, respectively) ever reported to date in OMZs at the center of the eddies. The $\delta^{18}$O of NO\textsubscript{3}\textsuperscript{-} also became highly enriched. The isotopic composition of NO\textsubscript{3}\textsuperscript{-} and NO\textsubscript{2}\textsuperscript{-} provides important information about the nature and degree of N loss processes since organisms generally preferentially use the lighter isotopes ($^{14}$N, $^{16}$O), leaving the substrate enriched in heavier isotopes ($^{15}$N, $^{18}$O). Large isotope effects have been associated with the first steps of denitrification, i.e. NO\textsubscript{3}\textsuperscript{-} and NO\textsubscript{2}\textsuperscript{-} reduction (15-30% and 5-25%, respectively). Biogenic N\textsubscript{2} excess was also the highest in the centers of the eddies (up to near $\sim$20 $\mu$mol/kg), where $\delta^{15}$N-N\textsubscript{2} also increased concurrently as more N\textsubscript{2} was produced.

We are currently analyzing samples from the M91 cruise, where the most coastal of the eddies monitored during the M90 cruise was revisited, allowing us to better understand
the temporal evolution of these eddies and mechanisms that lead to extreme fixed N loss in these deep ocean features.

**Best practices for autonomous measurements of seawater pH with the Honeywell Durafet**

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In situ performance of autonomous pH sensors is examined by comparing co-located pH, O₂, and pCO₂ sensors. In the absence of frequent contemporaneous discrete samples, regional empirical relationships are used to examine data quality. Due to unrefined shore-side calibration protocols and variable conditioning periods for pH electrodes, sensors are often calibrated to an independent determination of pH made alongside the sensor during a deployment. These in situ calibration and quality control (QC) procedures are examined here in order to determine the errors associated with different approaches and lay the groundwork for best practices. Sensor packages employing the Honeywell Durafet remained stable across multiple deployments for over nine months. However, sensor performance is often limited by biofouling. Regional empirical relationships for estimating carbonate system parameters are shown to enable identification of otherwise indistinguishable sensor offset and drift when multiple sensor types are co-located. Our results indicate that the Durafet is capable of stable pH measurement, relative to a chosen reference, of better than 0.04 pH units over multiple months. Accuracy can be improved where a robust shore-side calibration is performed along with an independent means data QC throughout a deployment and where the effects of biofouling are not the dominant source of error. This work explores pH sensor quality control (QC) procedures based on ancillary sensor and bottle data.

**Observed dominance of submesoscale fronts to subtropical chlorophyll**

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It has been suggested that intermittent forcing by mesoscale eddies of size 10-100 km could account for a significant fraction of the annual nutrient requirement in the oligotrophic waters of the North Atlantic. However quantitative agreement on eddies contribution has not been achieved and theoretical and numerical studies suggest that
submesoscale features of size 1-10 km and frontal process may play a leading role in vertical nutrient transport. In this study, we utilize multiple satellite products, including SSH, SST and ocean color chlorophyll at different scales, to offer the first observational evidence that submesoscale frontal features are associated with the largest fraction of chlorophyll biomass and anomaly variability in North Atlantic oligotrophic waters. These findings support the conclusions of previous idealized modeling studies that submesoscale physics are the missing link in the nutrient budget.

By separating the identified physical features (eddy core, eddy edge and elongated fonts) into groups with positive vorticity ($\zeta^+$) and negative vorticity ($\zeta^-$), we show that chlorophyll are more co-incident with $\zeta^-$ features as spatial resolution becomes finer, which can be directly related with frontogenesis process. We also found that during spring bloom, chlorophyll is more co-incident with cyclonic eddies and fronts of $\zeta^+$ than other periods from year 2010 to 2012, suggesting that when upper surface nutrients are plentiful, eddy-pumping mechanism is more important compare to summertime when nutrients are depleted due to surface warming and strong stratification. Pure stirring cannot explain these scale-dependent and seasonal patterns, and we proposed two possible mechanisms.

**Plankton resonant response to light and nutrients in mesoscale vortices**

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The response of a fully-recycling ecosystem to light and nutrients variability within mesoscale cyclones is numerically investigated. To this end, a simple physical-ecological coupled model is constructed where mesoscale forcing is introduced in terms of vertical displacement of isopycnals in a NPZ (Nutrients-Phytoplankton-Zooplankton) model. Additionally, small-scale motion is parametrized as a Fickian-type diffusion along isopycnals. We observe that stationary stable ecological solutions are possible within mesoscale vortices with non-zero P and Z profiles. The dependence of these solutions on small-scale motion, vortex intensity, and trophic regime is explored. Firstly, small-scale motion increase the spatially integrated P biomass at a characteristic diffusion coefficient K*, at which resonance between phytoplankton and diffusive timescales occurs. Two mechanisms are involved in this P increase, namely nutrients uplift to lighter levels and Z grazing pressure decrease. Secondly, vortex intensity exerts a double effect on the ecosystem. On the one hand, it enhances the irradiance affecting isopycnals, which induces a positive linear response in P. On the other hand, it increases the diffusive fluxes. As a result, K* is unaffected by vortex intensity, that is, the P enhancements caused by isopycnal doming and small-scale motions are approximately additive. Finally, the trophic regime determines the magnitude of the ecosystem response. The increase in P biomass caused by small-scale motion is significant only in mesotrophic regimes, and it remains independent of the trophic condition when the vortex intensity varies.
Employing continuous *in situ* measurements of dissolved O$_2$/Ar in the Arctic Ocean, we seek to assess the mechanisms controlling the physical and biological oxygen saturation state variability in the surface ocean beneath sea ice and in ice-free conditions. O$_2$/Ar measurements were made underway at 8 m depth using Equilibrator Inlet Mass Spectrometry (EIMS) across the Eurasian Basin from August-October 2011. We parse out the biological oxygen saturation and Ar saturation using concurrently collected optode measurements of total O$_2$, providing us with an unprecedented resolution of Ar saturation state.

In the surface water under sea ice cover, Ar shows strong regions of undersaturation in the marginal ice zone (MIZ) reaching -6%. Poleward of the MIZ where sea-ice concentrations are higher, Ar is supersaturated up to 4%. Beneath ice cover, biological oxygen supersaturation averages 4.9% with distinct peaks of 18% and 13% within 500 km of the MIZ as well as several intermediate peaks beneath the ice. In ice-free conditions on the Siberian shelf, both gas signals are near equilibrium.

Spectral slopes of Ar and O$_2$/Ar were -2 and -3 respectively for horizontal wavelengths of 2-200 km, suggesting differing scales of variability between the physics and biology. Wavelet analyses also reveal variations in energy content across different wavelengths between under ice and ice-free conditions.

We investigated temperature, salinity, and melt water to evaluate the controls on Ar saturation variability. Undersaturation is not consistent with trends in salinity and while cooling of water as it moves under the ice is a possible contributor to undersaturation, preliminary calculations indicate that the currents are too slow to account for the signal we observed. Changing atmospheric pressure is another potential mechanism, which we will investigate by accounting for pressure history over the residence time of the gas in the ocean surface. Despite contradictory results from preliminary melt water assessment, influx of Ar undersaturated melt water still remains as a leading hypothesis for the cause of undersaturation. Supersaturation in the interior basin is not likely due to bubble processes, increasing salinity or warming but could be a result of sea-ice freezing, decreasing atmospheric pressure or mixing of Pacific and Atlantic water masses. Future work will investigate these possible controls.
Carbon isotopes are one of the most effective tools we have to understand the sources, composition and cycling timescales of dissolved organic carbon (DOC) in the ocean. The past decade has seen an evolution of isotope measurements from bulk techniques to analyses targeted at specific fractions and molecular components of DOC. We have expanded this approach by coupling ultraviolet oxidation analysis of whole seawater with inverse numerical techniques to estimate the distribution of carbon isotopes within DOC. Our analyses suggest that up to 30% of DOC in the deep ocean consists of a semi-labile fraction with a turnover time less than 50 years. These results provide a mechanism for both the anomalous ageing of DOC in the deep Southern Ocean, and deep sea gradients in DOC concentration.

Increases in dissolved inorganic carbon at all depths measured in the eastern North Atlantic from 1989 to 2012: the Extended Ellett Line

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The Extended Ellett Line (EEL) is an oceanographic transect running from Scotland to Iceland via the Rockall plateau, where repeated measurements of physical oceanographic parameters have been made since 1975. It captures the flow of warm, salty water from the eastern North Atlantic into the Nordic Seas and around half the returning deep, cold current, important components of the Atlantic Meridional Overturning Circulation. Water masses crossed by the EEL include East North Atlantic Water, Sub-Polar Mode Water, Intermediate Water, Labrador Sea Water, Iceland-Scotland Overflow Water and Lower Deep Water.

Recently, high-quality biogeochemical datasets have been collected on the EEL, including marine carbonate system measurements. These data have been combined with data from the CARINA (CARbon IN the Atlantic Ocean) synthesis to reveal measurable increases in Dissolved Inorganic Carbon (DIC) at all depths along the transect from 1989—2012, by comparing average DIC at an array of neutral density (\(\gamma^n\)) intervals between years. The maximum rate of increase is 2.7 \(\mu\text{mol kg}^{-1} \text{yr}^{-1}\) found in the interval \(26.80 \leq \gamma^n < 26.90 \text{ kg m}^{-3}\), and the rate of increase in general decreases with depth. There is no significant change in measured Total Alkalinity (TA) apparent, and a corresponding decrease in pH (calculated from DIC and TA), which reaches a maximum of 0.013 pH units yr\(^{-1}\) in the interval \(\gamma^n < 26.60 \text{ kg m}^{-3}\), the surface layer. These changes could have resulted from the addition of anthropogenic CO\(_2\) to the ocean via the atmosphere, variability in biological uptake of CO\(_2\) in the surface ocean and its sequestration to depth, and alterations to ocean circulation.

In 2012, samples were collected on the EEL for \(\delta^{13}C\) of DIC, and most of these results are illustrated. These data will provide a useful baseline for future studies in this region, as there is a lack of existing historical data to carry out similar analyses as for DIC and
other carbonate system parameters. The $\delta^{13}$C of DIC is affected by anthropogenic input of isotopically light CO$_2$ (the Suess effect) and also by biological activity. The magnitude of the anthropogenic change in $\delta^{13}$C of DIC relative to its natural seasonal and interannual variability is an order of magnitude greater than for DIC as a whole.

The EEL time-series forms part of UK climate monitoring strategy, and is maintained by the UK National Oceanography Centre and the Scottish Association for Marine Science, with core funding provided by the UK National Environment Research Council. As such, it is sure to be occupied many more times over the coming years, supplying additional biogeochemical data to extend the analysis illustrated here.

Microbial autotrophic and heterotrophic carbon cycles within oxyclines during seasonal oxygen transition in the Chesapeake Bay

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Seasonal oxygen depletion is a common feature of eutrophic ecosystems and causes a succession of microbial community composition and processes. Here we report the variability of microbial metabolism in and around oxic/anoxic interface using changes of dissolved inorganic carbon (DIC) in the mesohaline region of Chesapeake Bay in 2010 and 2011. Microbial processes were characterized by high DIC production (i.e. respiration) and DIC consumption (i.e. autotrophic fixation other than by phytoplankton) in and around pycnoclines in mid-summer. In addition, high DIC fixation below the pycnocline was observed during the transition of bottom water from oxic to anoxic and vice versa. The variability was highly related to a temporal and spatial gradient of nitrogen species. Our data suggest that anaerobic metabolism in oxic/anoxic interface and transition period can play an important role in net ecosystem metabolism. We hypothesized that stratification enhanced the production of chemolithoautotroph and anoxygenic photoautotroph which may serve as additional energy source.

Partitioning phytoplankton carbon biomass into three size groups using satellite ocean colour observations

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In the recent years, phytoplankton functional types (PFTs) have been added to the growing list of products of ocean colour remote sensing. PFTs are the groups of phytoplankton that play a specific prominent role in the biogeochemical cycling and the functioning of marine ecosystems. Methods for deriving PFTs from remote sensing differ
both in what remotely sensed variable they are based on (e.g. absorption, chlorophyll concentration, particulate backscattering) and what criterion they use to define PFTs (taxonomy or cell size). Here, we employ a PFT method that uses particulate backscattering retrievals and Mie modelling to derive the parameters of particle size distribution [Kostadinov et al., 2009, 2010] and retrieve three PFTs defined by the size of cells: picophytoplankton (having equivalent spherical diameter between 0.2 and 2 µm), nanophytoplankton (2–20 µm) and microphytoplankton (20–50 µm). Kostadinov et al. [2009, 2010] expressed the PFTs in terms of relative contribution to biovolume concentration (i.e. the total volume of cells per unit volume of seawater). However, a more useful way to express the PFTs would be to present them in terms of carbon biomass, since this quantity is more closely related to climate and is of great interest both for biogeochemical/ecosystem modellers and for deriving phytoplankton productivity from remote sensing [e.g. Behrenfeld et al., 2005]. This motivates us to develop a procedure for recasting of the PFTs from the original method in the form of carbon biomass, using quantitative relationships between phytoplankton cell volume and cellular carbon content, reported by Menden-Deuer and Lessard [2000], after the initial effort by Kostadinov [2009]. We present the preliminary results of this carbon-based partitioning of the PFTs based on global data from the Sea-viewing Wide Field-of-view Sensor (SeaWiFS).

The CARIACO ocean time-series program: Long-term observations of key carbon fluxes in a tropical continental margin

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Systematic estimates of the vertical export of primary production from surface waters to the deep ocean over long periods of time are of key importance to accurately assess changes in carbon budgets in the ocean. The CARIACO Ocean Time-Series Program has been providing estimates of the variability in surface production, consumption, and transformations of various forms of carbon in the Cariaco Basin, Venezuela, for the past 18 years. This variability is linked to large-scale processes in the Atlantic Ocean which affect climate-scale records of carbon fluxes and of ecological processes recorded in the sediments. The oceanography of the Cariaco Basin is influenced by the Intertropical Convergence Zone (ITCZ). Between December and May, the Cariaco Basin experiences
dry, upwelling-favorable weather. This leads to primary production of ~1.4 g C m$^{-2}$ d$^{-1}$ (upper 100 m). From June to November is the rainy season, winds are weaker and upwelling is reduced; primary production falls to half the rate observed during upwelling. This is reflected in the magnitude of particulate organic carbon (POC) export from the euphotic zone (Ez). Sampling conducted over three years using drifting sediment traps at 50 and 100 m revealed that POC fluxes from the base of the Ez (about 50 m) were higher during upwelling ($0.62 \pm 0.16$ g C m$^{-2}$ d$^{-1}$ vs. $0.31 \pm 0.09$ g C m$^{-2}$ d$^{-1}$ during non-upwelling). The ratio of this POC export at the base of the Ez to net primary production (NPP) was ~20-40% and did not seem to have a seasonal variation.

Export production is disconnected from primary production in Cariaco. Transfer efficiency estimates ($T_{100}$=POC flux 100 m below the base of the Ez / POC flux at the base of Ez) were lower (< 20%) than those measured in open ocean oligotrophic waters (> 30%), indicating high POC degradation rates in the upper 100 m in Cariaco. Additionally, POC fluxes measured at 200 m with moored traps were < 10% of those measured at the base of the Ez. POC fluxes in the twilight zone (225 and 410 m) are an order of magnitude lower than those observed within the upper 100 m. This difference is due to rapid consumption by zooplankton and remineralization by bacteria and dissolution. Deeper (> 200 m) settling POC fluxes don’t covary with those in the upper 100 m, likely due to strong lateral advection. Export production is correlated with week-long region-wide averages of satellite-derived chlorophyll a (Chla) estimates, but not with the single monthly in situ Chla measurements. This suggests that export production is more a reflection of larger-scale processes and is not driven by daily, short-scale changes in surface Chla.

Over the 18 years of the time-series, significant changes in carbon production and fluxes have been observed. Due to a decrease of the Trade Winds intensity in the Caribbean over the last two decades, which has led to a decrease in upwelling intensity, a decrease of 20-40% in NPP has been observed at CARIACO, accompanied by a shift in the phytoplankton community from larger to smaller cells, and an increase in biomass of zooplankton. POC fluxes have also varied, but their intrinsic connection to mineral ballast ultimately regulates the export of POC from the euphotic zone. As the time-series continues to gather valuable measurements of key carbon parameters, a clearer understanding of the factors that regulate the variability and vertical export of net primary production (NPP) from surface waters to the deep ocean will be gained. The Cariaco Basin stores one of the most extraordinary sedimentary records of paleoclimate variations available. Understanding the relationship between export production, NPP, and how changes in the ecology and biogeochemistry of this basin reflect changes in the Atlantic Ocean is important for reconstructions of past conditions on our planet.

**Carbon dioxide and water quality time-series observations at Gray’s Reef National Marine Sanctuary**

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Ocean acidification, a decrease in seawater pH (acidity scale) caused by the increase of anthropogenic (human-induced) carbon dioxide (CO₂) into the atmosphere, has received considerable attention in recent years. As scientists gain an understanding of the adverse effects of increased CO₂ and decreased pH, a major concern of ocean acidification is the impact to organisms, which use calcium to build their bones, skeletons or other structural components. Recent research has indicated that the oceans act as a net repository or “sink” for atmospheric CO₂, but that this sink is not uniform worldwide. Many coastal regions oscillate between being a CO₂ sink and source depending on the time of year. The effects of ocean acidification have yet to be fully understood in coastal regions where biogeochemical processes are often vastly different from regions dominated by upwelling.

The coastal areas surrounding our continent are known to play a considerable role in determining global carbon cycling; however, little has been done to determine input from the coastal margins towards the total carbon “budget.” Insufficient data exists to adequately determine the natural fluctuation (“flux”) of air-sea CO₂ with any level of confidence, but progress is being made. The ability to explain the control mechanisms driving the variability of coastal partial pressure of CO₂ (pCO₂ or the concentration of CO₂ in seawater) and pH is limited. Understanding these control mechanisms and how they affect pCO₂ and pH is essential to predicting future changes in CO₂ flux, pH and carbonate saturation in our oceans. The primary reason that scientists are not able to determine the control mechanisms for coastal ocean regions is the absence of long-term high-resolution data, but progress is being made to resolve this issue. The highly dynamic coastal margin, with its combined terrestrial and oceanic input makes understanding this region a necessity for determining what mechanisms control the fluctuation of carbon dioxide.

**Carbon budget for the Gulf of Maine from time-series data sets**

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Despite covering a small fraction of the earth’s surface, coastal margins play a significant role in the global carbon cycle due to the fact that margin rates of carbon fixation, remineralization and burial are much greater than global averages. The Gulf of Maine, a semi-enclosed shelf sea, is a substantial contributor to the total carbon budget of the east coast margin largely due to the gulf's high level of biological productivity. As part of the NACP Coastal Synthesis Project/East Coast, we compiled water column fluxes, resuspension and offshore advection and sediment accumulation rates of particulate organic carbon (POC) to produce annual and region-based estimates of POC export and burial. Our synthesis results indicate that even though a majority of the surface-produced, sinking POC is rapidly remineralized in the relatively shallow Gulf of Maine...
water column, sedimentary carbon accumulation is significantly larger than that reported for the Mid- and South Atlantic Bight regions. Additionally, a substantial carbon inventory exists in the pervasive and thick benthic nepheloid layers in the Gulf of Maine. Lateral movement of the bottom nepheloid layers to the adjacent deep North Atlantic slope represents a potential offshore input of 4 Tg C per year.

Recently we collected time-series data of near-bottom and surface pCO$_2$, salinity, temperature, dissolved oxygen, and beam attenuation at an 85 m-deep site in the western gulf. Total alkalinity, calculated pH, and estimated aragonite saturation levels show a close temporal coupling between the surface and deep-water pCO$_2$. The data suggest that aragonite acidification in the gulf is driven by seasonal algal carbon export and remineralization in the near-bottom nepheloid layers. We examine the Gulf of Maine carbon budget relative to other east coast regions and consider the impact of acidification on the gulf's seasonal CO$_2$ cycle.

**Characterization of phytoplankton size and taxonomic composition by shipboard streak imaging multivariate optical computing (SSIMOC)**

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Characterization of phytoplankton community composition, and how it varies in time and space, is critical to our understanding of biogeochemical cycles in the ocean. Instruments for phytoplankton characterization currently on the market have either limited discrimination ability (e.g., they cannot differentiate between similarly-pigmented species) or have power demands that require connection to a shore-based power supply. Our overall goal, therefore, is to design and construct an instrument for the in situ characterization of phytoplankton size and taxonomic composition that has excellent classification ability, low power requirements, and that is small enough in size to be deployed on moorings or on autonomous underwater vehicles like gliders. The Shipboard Streak Imaging Multivariate Optical Computing Instrument, or SSIMOC instrument, represents an intermediate milestone in our overall goal. This ship-based instrument has good (but not yet excellent) classification ability and very low power consumption. It can count, classify, and quantify the size of phytoplankton cells in the range of 2 to ~ 50 $\mu$m. The SSIMOC currently sits on a 2’ x 3’ breadboard; future work will focus on a reduction in instrument size and on improvements to pattern recognition algorithms. Key components of the SSIMOC instrument are interference filters called Multivariate Optical Elements (MOEs). The design of each MOE incorporates data from high resolution fluorescence excitation spectra such that the transmission spectrum of each MOE reproduces one linear discriminant function required for phytoplankton classification. When a target phytoplankton cell is excited by light filtered through an MOE, the fluorescence response produces a streak that is captured by a small digital camera. The
intensity of fluorescence (normalized to a neutral density filter) codes for the phytoplankton species; the width of each streak is proportional to the size of the cell. We have designed several sets of MOEs and have tested the SSIMOC instrument on 5 occasions using samples collected at Martha’s Vineyard Coastal Observatory (MVCO). We have compared SSIMOC instrument output to that of the Flow Cytobot and the Imaging Flow Cytobot instruments deployed at MVCO by the Sosik lab. Want to know the results? Come by to see the poster!

Export Processes in the Ocean from Remote Sensing (EXPORTS) - Planning a NASA Field Campaign

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A major goal of NASA satellite ocean color missions is to constrain carbon cycling over the global ocean. A fundamental difficulty is that satellite remote sensing provides only a measure of ocean color (the spectrum of sunlight reflected back from the water column) and not carbon cycle-relevant concentrations or rates. Linking ocean color observations to carbon cycling objectives requires intensive field observations in which both remotely sensible and carbon cycle parameters are measured simultaneously. This poster describes the planning process for a major NASA field effort aimed at predicting the consequences of changing plankton patterns on the strength and efficiency of the biological pump - the "EXport Processes in the Ocean from RemoTe Sensing (EXPORTS)". Goals, objectives, scientific questions, experimental approach and experimental plans for EXPORTS will be presented. The goal of this poster is to get feedback from the community for this scoping exercise.

Carbon and \(^{234}\text{Th}\) Thorium fluxes associated with a deep-water front in the California Current Ecosystem Long-Term Ecological Research site

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Frontal regions are common in the California Current System (CCS) and are often sites of increased upwelling, downwelling, and biological production. Therefore, they likely play an important role in the biological pump as organic matter is transported to depth either on sinking particles or during subduction of both POM and DOM. To assess the importance of enhanced gravitational flux in frontal regions we made \(^{234}\text{Th}:^{238}\text{U}\) disequilibrium measurements during rapid sampling transects on the August 2012 cruise of the California Current Ecosystem Long-Term Ecological Research program.
Preliminary results show a strong gradient in $^{234}$Th deficiency at the front, which could be the result of high export on the cold side of the front. Vertical profiles show that the depth of maximum deficiency increased on the warm side of the front, which could be indicative either of export production deeper in the water column or subduction of $^{234}$Th depleted surface waters from the cold side of the front.

**Calibrating the Deep Sea Durafet**

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The Deep Sea Durafet (DSD) is a potentiometric pH sensor consisting of an ion sensitive field effect transistor (ISFET) and a chloride ion selective electrode (Cl-ISE). This sensor is capable of making high frequency (> 1Hz) measurements up to 2000 dBar, and has been successfully integrated onto profiling floats. The number of floats equipped with the DSD is expected to increase significantly in the next several years, thus the establishment of a calibration protocol is essential to create a coherent pH dataset from profiling floats. Here, we present the effects of temperature, pressure, hydrogen ion activity, and chloride ion activity (analogous to salinity) on the response of the sensor. The results indicate that the sensor has an ideal response to hydrogen ion, and a near-ideal response to chloride ion activity, and is repeatable. Temperature and pressure response can be adequately described by simple empirical functions. Preliminary results show that the DSD can achieve a pH accuracy of 0.01, and repeatability approaching 0.001.

**Synthesis of observed air-sea CO\(_2\) exchange fluxes in the river-dominated East China Sea and improved estimates of annual and seasonal net mean fluxes**

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Limited observations exist for reliable assessment of annual CO\(_2\) uptake that takes into consideration the strong seasonal variation in the river-dominated East China Sea (ECS). Here we explore seasonally representative CO\(_2\) uptakes by the whole East China Sea derived from observations over a 14-year period. We firstly identified the biological sequestration of CO\(_2\) taking place in the highly productive, nutrient-enriched Changjiang river plume, dictated by the Changjiang river discharge in warm seasons. We have therefore established an empirical algorithm as a function of sea surface temperature (SST) and Changjiang river discharge (CRD) for predicting sea surface $p$CO\(_2\). Synthesis based on both observation and model show that the annually averaged CO\(_2\) uptake from
atmosphere during 1998-2011 was constrained to about 1.9 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 -3.0, -1.0, -0.9 and -2.5 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-early fall. The weak sink status during warm periods in summer-fall is fairly sensitive to changes of \(p\)CO\(_2\) and may easily shift from a sink to a source altered by environmental changes under climate change and anthropogenic forcing.

Multi-scalar particle dynamics at Station ALOHA with an aside regarding the influence of colored dissolved organic material on chlorophyll retrievals

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Beginning in September 2009, monthly profiles of particle load and particle size distributions (PSDs) have been collected at Station ALOHA, the sentinel time-series station for the oligotrophic subtropical North Pacific. In the summer of 2012, between May and September, high temporal resolution profiles (daily with gaps between cruises) of PSDs were collected in order to examine the temporal variability of particle size at Station ALOHA. Local variability in the PSD can be indicative of shifts in the community structure of marine microbes (phytoplankton and non-photosynthetic bacteria), reveal patterns in cell growth, and show grazing by zooplankton. The PSD also plays a central role in particle export by influencing settling speed. Satellite-based models of marine primary productivity often rely on aspects of photophysiology that are directly related to community size structure. We will present the time-series of PSDs as a function of depth and relate this data to community structure and phytoplankton diversity as gleaned from flow cytometry over daily to interannual time-scales. In addition, we will present preliminary findings related to the influence of color dissolved organic material on chlorophyll retrievals from space.

Variability of sea surface pCO\(_2\) and CO\(_2\) flux in the North Pacific

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The ocean plays an important role in regulating global carbon cycle by taking up and releasing CO\(_2\) from and to the atmosphere simultaneously. Variability of upper ocean carbon cycle in the north Pacific is investigated by using a coupled physical-biogeochemical model during 1958-2010 period. Comparisons with in-situ data from five contrasting oceanographic environments in the South China Sea, Monterey Bay, north
Pacific gyre, northwestern Pacific, and Gulf of Alaska suggest that the model is able to capture observed seasonal and interannual variability in sea surface pCO$_2$ and sea-air CO$_2$ flux. Seasonal variability of pCO$_2$ and CO$_2$ flux in the north Pacific follow SST changes closely with high and low values in summer and winter, respectively. On interannual and decadal scales, sea surface pCO$_2$ is primarily controlled by anthropogenic CO$_2$, followed by modulations from the El Niño-Southern Oscillation (ENSO) and the Pacific Decadal Oscillation (PDO), while sea-air CO$_2$ flux is significantly regulated by the PDO and the North Pacific Gyre Oscillation (NPGO).

Assess and project impacts of human activity and climate change on carbon and nutrient dynamics in the Gulf of Mexico

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A three-dimensional coupled physical-biogeochemical model is applied to simulate and examine temporal and spatial variability of circulation and biogeochemical cycling 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 input from major rivers. A 7-year model hindcast (2004–2010) was performed, and validated against satellite observed sea surface height, surface chlorophyll, and in-situ observations including coastal sea-level, ocean temperature, salinity, and nutrient concentration. The model hindcast revealed clear seasonality in nutrient, phytoplankton and zooplankton distributions in the GoM. In addition to the ecosystem dynamics, model simulated mean pCO$_2$ fields reproduce general features observed by satellite and in situ ship surveys, suggesting this coupled prognostic modeling system is promising for delineating the spatial and temporal variability of ocean material property distributions, and for quantifying air-sea and cross-shelf exchanges of carbon. The goal of this research is to develop an integrated modeling suite focusing on the Mississippi-Atchafalaya River basin and the GoM as a testbed. This coupled terrestrial-ocean ecosystem model suite will be unitized to examine processes controlling fluxes on land, their coupling to riverine systems, the delivery of materials to estuaries and the coastal ocean, and the associated marine ecosystem responses.
Session 2. Evolutionary responses of plankton to climate change

A new Gordon Research Conference on Ocean Global Change Biology

Dave Hutchins\(^1\) (chair), Phil Boyd\(^2\) (vice-chair), Adina Paytan\(^3\), and Shannon Meseck\(^4\) (co-organizers)

1. University of Southern California
2. University of Otago, New Zealand
3. Stanford University
4. NOAA/NMFS

We invite the OCB research community to participate in the upcoming first Gordon Research Conference on “Ocean global change biology” to be held July 6-11, 2104 at the Waterville Valley Resort, NH. This new GRC was created due to a growing awareness that our ability to predict biological responses to anthropogenic alteration of the oceanic environment demands that we address the interactive effects between distinct changing environmental factors. In the last decade our research community has primarily focused on the biological effects of changes to individual ocean properties, such as pH (ocean acidification) or temperature (sea surface warming). This GRC will bring these distinct but related research threads together by adopting a holistic approach to two pressing research questions – “How will ocean biota respond to fundamental and concurrent alterations of their environment?”, and “How will their cumulative responses affect ocean productivity, biodiversity and biogeochemistry?”. The aim of this new GRC will be to bring together disparate research communities, from experimentalists to modelers and from new students to senior investigators, who are all tackling aspects of biological responses to ocean global change. Sessions will include “A changing ocean environment”, “Paleo proxies for multiple environmental stressors”, “Adaptation and evolution”, “Ocean acidification effects on nutrients and trace metal supply”, “The interplay between warming, ocean acidification and ocean hypoxia”, “Interactive effects- evidence of biological synergism and antagonisms”, “Remote sensing and ecosystem modeling of multiple environmental stressors”, “Physiological basis for interactions between anthropogenic stressors”, and “The socio-economic impacts of ocean acidification”. This GRC is intended to help the marine science community to devise a range of interdisciplinary approaches to investigate the full complexities of biological responses to a broadly changing ocean environment.

Modelling responses in mesocosm food web succession to changes in nutrient stoichiometry

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We combine an optimality based chain model (Pahlow et al., 2013) with an optimal
current feeding model (Pahlow & Prowe, 2010). We consider three different configurations with two to four functional groups, a nutrient, phytoplankton, and herbivorous and carnivorous zooplankton, to analyse plankton-related processes. We validate our model with observations from mesocosm experiments (Hauss et al., 2012; Franz et al., 2012).

The first configuration (NP) contains only the nutrient and phytoplankton. Parameters were adjusted to represent a phytoplankton species adapted to nutrient-impoverished conditions. This configuration reproduces only the first half of the mesocosm experiment but, contrary to the observations, nutrients become exhausted as the model runs into a stationary phase towards the end of the simulation. This points to the importance of remineralisation and top-down processes, which are not included in the NP-configuration.

The second configuration is a nutrient-phytoplankton-zooplankton model (NPZ). The NPZ-model behaviour was analysed for parametrisations representing copepods, ciliates and dinoflagellates, according to Pahlow & Prowe (2010). Only ciliate parameters resulted in an acceptable agreement between model and observations during the first two-thirds of the simulations, which is encouraging as copepods were not present in the mesocosms. Without additional parameter tuning, this configuration tends to overestimate zooplankton and underestimate phytoplankton towards the end of the experiments.

We construct the third configuration (NPZC) by adding a second, carnivorous zooplankton compartment (C), preying on the herbivore introduced in the second configuration. The carnivore behaviour is described with the same (ciliate) parameters as the herbivore. The NPZC configuration provides a good representation of the whole time-course of the mesocosm experiments, although the nutrient concentration is still somewhat low towards the end of the simulations.

We conclude that three trophic levels, phytoplankton, herbivores, and carnivores, are required in the model in order to reproduce the observed behaviour of these mesocosm experiments. We propose that the major remineralisation- and higher trophic level-processes were due to ciliates.

**On the potential role of marine calcifiers in glacial-interglacial dynamics**

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Ice-core measurements have revealed a highly asymmetric cycle in Antarctic temperature and atmospheric CO2 over the last 800,000 years. Both CO2 and temperature decrease over 100,000 years going into a glacial period, then rise steeply over less than 10,000
years at the end of a glacial. There does not yet exist wide agreement about the causes of this cycle or about the origin of its shape. Here, we explore the possibility that an ecologically driven oscillator plays a role in the dynamics. A conceptual model describing the interaction between calcifying plankton and ocean alkalinity shows interesting features: (i) it generates an oscillation in atmospheric CO$_2$ with the characteristic asymmetric shape observed in the ice-core record, (ii) the system can transform a sinusoidal Milankovitch forcing into a sawtooth-shaped output, and (iii) there are spikes of enhanced calcifier productivity at the glacial-interglacial transitions, consistent with several sedimentary records. This suggests that ecological processes might play an active role in the observed glacial-interglacial cycles.

Seasonality, interannual variability, and multi-year trends in phytoplankton of the New England Shelf

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Interdisciplinary time series observations have unique potential to provide new insights into the controls on coastal phytoplankton communities. We are taking advantage of new 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 high resolution (~hourly) multi-year time series of taxonomically resolved phytoplankton acquired with FlowCytobot (FCB) and Imaging FlowCytobot (IFCB), custom-built automated submersible flow cytometers optimized for measurement of picoplankton and microplankton, respectively. Results from these ongoing 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. In particular, picophytoplankton (especially picocyanobacteria) are most abundant in summer and have been increasing in biomass over the last decade, at the same time that the relative contribution of nanophytoplankton has been declining. The microphytoplankton are dominated by diatoms, which typically bloom in fall and winter, and persist despite environmental extremes such as the warmest winter on record in 2012. Preliminary evidence suggests relatively stable winter time diatom biomass may be associated with high biodiversity and species-specific responses to interannual environmental variability.

Session 3. Trace element-biota interactions

Fe ligands produced by *Prochlorococcus*

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Many biologically important trace metals, such as Fe, are insoluble in oxic seawater. Marine microbes produce organic ligands that bind Fe and play an important role in determining how much Fe from dust, rivers and hydrothermal vents dissolves and stays in solution as part of the standing stock that is available to the microbial community. Determining the source organisms and chemical composition of these ligands, particularly in regions where Fe is a limiting nutrient, is important for understanding the bioavailability and cycling of iron. Our latest findings suggest that *Prochlorococcus*, one of the dominant photoautotrophs in the oligotrophic ocean, is capable of producing Fe ligands in culture. Liquid chromatography tandem inductively coupled plasma mass spectrometry was used to separate and detect ligands from the culture media of six strains of *Prochlorococcus*. All of these strains were capable of producing two to three different Fe ligands, yet no two strains produce the same suite of ligands. Our goal is to structurally characterize these ligands and determine whether they play a role in *Prochlorococcus* Fe uptake or if they make up part of the Fe ligand pool in regions of the ocean where *Prochlorococcus* dominate.

**Interactive effects of CO$_2$ and trace metals on the proteasomal activity, metabolism and stress response of marine bivalves *Crassostrea virginica* and *Mercenaria mercenaria***

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Increased anthropogenic emission of CO$_2$ changes the carbonate chemistry and decreases the pH of the ocean, which can affect the speciation and bioavailability of metals in polluted habitats such as estuaries. However, the effects of acidification on metal accumulation and stress response in estuarine organisms including bivalves are poorly understood. We studied the interactive effects of CO$_2$ and two common pollutants copper (Cu) and cadmium (Cd) on metal accumulation, ATP/ubiquitin-dependent intracellular protein degradation, stress response and energy metabolism in two common estuarine bivalves - *Crassostrea virginica* (eastern oyster) and *Mercenaria mercenaria* (hard shell clam). Bivalves were exposed for 30 days to clean seawater (control) and to either 50 µg L$^{-1}$ Cu or 50 µg L$^{-1}$ Cd at one of the three partial pressures of CO$_2$ ($p$CO$_2$): ~400, 800 and 1500 µatm representative of the present-day conditions and projections of the Intergovernmental Panel for Climate Change (IPCC) for the years 2100 and 2250, respectively. Clams accumulated lower metal burdens than oysters. Elevated $p$CO$_2$ enhanced Cd and Cu accumulation in mantle tissues of clams and oysters, and higher Cd and Cu burdens were associated with elevated mRNA expression of metal binding proteins (metallothionein and ferritin). Activities of three main catalytic centers of the
proteasome (responsible for chymotrypsin-, trypsin- and caspase-like activity) were differently affected by Cu and Cd exposure depending on $p$CO$_2$ indicating enhanced protein degradation and possibly a shift in the predominant protein substrates of the proteasome. Levels of mRNA transcripts for ubiquitin and a tumor suppressor p53 were suppressed by metal exposures in normocapnia but this effect was alleviated or reversed at elevated $p$CO$_2$. Exposure to 800 μatm $p$CO$_2$ and Cu significantly reduced muscle glycogen, cellular ATP and ADP levels in clams, whereas Cd-exposed oysters had significantly elevated cellular ATP levels under all $CO_2$ levels. Other combinations of metals and $CO_2$ levels had no effect on cellular energy status in clams or oysters. The data suggests that environmental $CO_2$ levels can modulate metal accumulation and toxicity in the studied bivalves in a species-specific manner, which can affect their fitness and survival during the global change in estuaries. Supported by NSF award IOS-0951079 and UNC Charlotte’s Faculty Research Grant.

The uptake of iron during spring and summer in the Irminger and Iceland Basin using carrier free $^{55}$Fe

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Iron as a limiting micronutrient controls the efficiency of the carbon pump in over 40% of the world’s oceans. Due to its crucial role in the food web, iron has received considerable attention in the past three decades, with emphasis on the dissolved fraction (dFe <0.2-0.45 mm). However, the bioavailability of iron, i.e. which fraction is taken up and incorporated into the cells, has received less attention. We report here for the first time on the application of a carrier-free $^{55}$Fe applied in situ in the high-latitude North Atlantic, a seasonally iron-limited region with deep water formation. The carrier-free $^{55}$Fe allowed for addition of pM concentrations of Fe with high activity. Studies were conducted over spring and summer 2010 and uptake was assessed between two size fractions, 0.2-5 μm and >5 μm. A shift was observed in the uptake with the >5 μm fraction dominating the uptake during spring while the smaller fraction dominated the uptake during summer. The results suggest that during spring it is the larger phytoplankton that dominate the bloom and potentially are exported, while during summer, smaller phytoplankton and bacteria dominate the post-bloom.

Iron limitation effects a massive shift in iron- and flavin-based antioxidant enzyme systems and their substrates in the chlorophyte alga *Dunaliella tertiolecta*
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Ubiquitous in the neritic ocean, it is now believed that iron-limitation is the most important factor controlling primary production in oceanic phytoplankton. To investigate the effects of iron deficiency, Dunaliella tertiolecta was cultured under limiting (100 nM Fe) and replete (1µM Fe) iron concentrations. The physiological status and the Water-Water antioxidant defense system were evaluated. Iron limitation effected a 21% drop in PSII efficiency (replete= 0.634± 0.012; limiting= 0.507± 0.012) concurrent with a 17.5% reduction in photosynthetic rates (replete= 265.8 umol O₂/mg chl/hr ± 5.7; limiting= 219.3 umol O₂/mg chl/hr ± 5.7). Both heme and non-heme based antioxidant enzyme activities were assessed. Heme-based Ascorbate peroxidase (APX), exhibits an 84% iron limited rate reduction (replete and limited = 36.23 and 5.72 umol ascorbate mg prot-1 hr-1 ±2.96, respectively). Conversely, the flavin-based Monodehydroascorbate reductase (MDHAR), exhibits a significant rate increase, 2.16±0.19 (replete) to 3.86±0.19 umol NADH mg prot-1 hr-1 under iron limitation. Iron deficient cultures exhibit a 34% increase in total available ascorbate. These investigations suggest that D. tertiolecta is able to maintain a stable growth rate under iron limitation by re-allocating its subcellular usage of available iron and increasing the availability of total ascorbate. Further investigations will determine the presence of additional iron/flavin based molecules involved in the photosynthetic apparatus and anti-oxidant scavenging mechanisms.

Session 4. Southern Ocean processes

Air-sea gas exchange revisited: Improving Southern Ocean carbon fluxes in a global biogeochemical model

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Air-sea gas exchange has been parameterized with a variety of wind speed dependencies, ranging from linear to cubic. The choice of an adequate formulation depends not only on the particular geographical situation but also, in case of ocean modeling applications, on the spatial and temporal resolution of the model and atmospheric boundary conditions. Here, we present a study that varies the air-sea gas exchange parameterizations in an eddying, full-depth, global-ocean configuration of the Massachusetts Institute of Technology general circulation model (MITgem) coupled to the MIT ecosystem model and to a marine carbon chemistry model. This particular model configuration was developed for NASA’s Carbon Monitoring System (CMS) and is known as ECCO2-Darwin. Our model results show that at the high spatial resolution of this model (18 km horizontal grid spacing) and the temporal resolution of the atmospheric forcing (6-hourly winds) quadratic formulations for the piston velocity lead to an over-estimation of carbon uptake, especially in high wind regions like the Southern Ocean. Not only does using a
linear parameterization (we used that of Krakauer et al., 2006) lower the overall carbon uptake in the Southern Ocean to more realistic values, it also diminishes the high frequency noise that spreads into simulations of atmospheric concentrations (visible for instance when comparing model simulations with observations at Palmer Station, Antarctica) and lowers the amplitude of the annual cycle of global CO₂ fluxes.

Fe transport from the Antarctic shelf and the impacts on phytoplankton blooms in the southern Scotia Sea

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Recent observations have identified a natural iron fertilization area over the shelf of Elephant Island, Antarctica, where the southern Antarctic Circumpolar Current (ACC) impinges upon the shelf and interacts with the shelf current leading to a strong off-shelf transport of Fe-rich shelf waters. Satellite and in-situ measurements suggest that this iron input sets the stage for massive phytoplankton blooms downstream in the southern Scotia Sea, one of the most productive regions in the Southern Ocean. In this presentation, we used a recently developed high-resolution (~2 km) regional coupled physical-biogeochemical model to investigate the Fe transport and dispersion, and the impacts of Fe offshore export on phytoplankton blooms in the southern Drake Passage and southern Scotia Sea. Model results suggest a coherent circulation in the Antarctic Peninsula shelf throughout the year that leads to persistent off-shelf export of shelf waters around Elephant Island, which is transported downstream by the southern ACC current and drives phytoplankton blooms in the southern Scotia Sea. Model results further suggest that the microbial loop and organic ligands produced by bacteria are important in keeping dissolved Fe within the surface layer over long-distances, hence sustaining the blooms. However, diatoms and meso-zooplankton (here including krill) dominate the biomass of phytoplankton and zooplankton, respectively, within the high Fe plume.

Biogeochemical variability in the Ross Sea: Results from a glider deployment

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The Ross Sea exhibits substantial biological productivity with a marked seasonal phytoplankton cycle. Partially as a result of the difficulty in obtaining in situ measurements in this remote high-latitude environment, small-scale biogeochemical variability in this region has not been well resolved and the influence of Modified Circumpolar Deep Water (MCDW) on productivity is poorly understood. In this study an analysis of high-resolution spatiotemporal data from an autonomous glider was used to delineate shifts in phytoplankton biomass and composition and highlight potential driving mechanisms. Glider measurements included temperature, salinity, oxygen, chlorophyll fluorescence, and optical backscatter, and were collected during the 2010-2011 austral summer. Backscatter and fluorescence observations were used to estimate particulate organic carbon (POC) and chlorophyll (Chl) along two nearly overlapping glider sections traversing Ross Bank. The POC:Chl ratio abruptly increased during the second transect. This shift suggests an abrupt spatial, and presumably temporal, transition between a *Phaeocystis antarctica*-dominated assemblage characterized by low POC:Chl ratios to a diatom- dominated assemblage. Higher POC:Chl ratios, suggestive of diatom-dominance, were not strongly correlated with the presence of MCDW or with shallower mixed layer depths. Instead, higher POC:Chl ratios were associated with higher temperatures and increased time since ice melt. These results highlight the need for high frequency, in situ data to resolve rapid assemblage shifts, with implications for remote sensing and modeling of biogeochemical parameters.

Spatiotemporal variability of satellite-derived chl-a along the West Antarctic Peninsula: Role of submarine canyons

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The West Antarctic Peninsula (WAP) is experiencing some of the most dramatic climate change on the planet, with rapid ocean-atmosphere warming, melting of coastal glaciers, and reductions in seasonal sea ice cover. Patterns observed from long-term monitoring sites reveal substantial bottom-up and top-down repercussions throughout the food web, with changes in nutrient and light availability for phytoplankton as well as changes in foraging capacity of ice-obligate predators such as Adélie penguins. However, ecosystem responses may vary in space and time as maritime conditions propagate poleward and interact with local physics and topography. On local scales, submarine canyons may act as conduits for warmer upper circumpolar deep water, reduce seasonal sea-ice concentrations and provide a reservoir of macro- and micronutrients. As a first step toward evaluating the effect of canyon-induced dynamics on local ecosystems, we combine high spatial resolution bathymetry with ~1-km resolution daily and 8-day
satellite ocean color data. Four canyons and adjacent shelf controls were defined as local regions with depths greater than 700 meters (or <200m for controls): North Anvers, Palmer Deep, Avian Island and Charcot Island, which became seasonally free of sea ice in 2008. Pixel percent retrieval was greater than 50% for the Palmer region (8-day) and > 70% for North Anvers and Avian Island regions. Although interannual variability is high and likely associated with larger scale wind, freshwater and sea-ice dynamics, initial analyses demonstrate statistically significant differences in chl-a between canyons and adjacent shelf regions. The canyon effect varies by season and region, with elevated chl-a above the canyons relative to the adjacent shelf associated with mid to late season blooms and lower latitudes. Thus, the use of ocean color metrics to extend inference from in situ time series is promising, even in polar latitudes associated with high cloud cover.

Optical properties and primary production in the Southern Ocean (SO GasEx)

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Optical properties and primary production were measured during the Southern Ocean Gas Exchange Experiment (SO GasEx; March-April, 2008). To assess and evaluate these properties derived from remote sensing, absorption coefficients derived from remote sensing reflectance ($R_{rs}$) with the Quasi–Analytical Algorithm (QAA) were compared with those from in situ measurements from both an ac9 optical instrument deployed on a profiling package and from discrete water samples analyzed using filter-pad spectrophotometry. Total absorption coefficients from $R_{rs}$ retrievals were found, on average, to be ~12% less than ac9 measurements and ~15% less than filter-pad measurements. Absorption coefficients of gelbstoff-detritus and phytoplankton pigments (at 443 nm) derived from $R_{rs}$ were ~15% and ~25% less than ac9 measurements, respectively. Further, incorporating measured surface radiation data, water-column primary production ($PP_{eu}$) was estimated using chlorophyll concentration based models (Chl-PP) and a phytoplankton absorption based model (Aph-PP), where remote-sensing Chl was retrieved with an operational empirical algorithm. These estimated $PP_{eu}$ values were then compared with primary productivity measured using $^{14}$C incubation techniques, and coefficient of determination ($R^2$, $N = 13$) of 0.74 were found for the Aph-PP results, while the $R^2$ of the Chl-PP results were less than 0.5. Such a contrast further highlights the importance of analytically retrieving phytoplankton absorption from measurement of ocean color and the advantage of using phytoplankton absorption to represent the role of phytoplankton in photosynthesis. Spatial distributions of $PP_{eu}$ in the greater SO GasEx region estimated from satellite data are also presented.

Response of phytoplankton to 21st century climate change in the Southern Ocean: an Earth System Model intercomparison

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We examine the Southern Ocean response of phytoplankton biomass, productivity and ecosystem composition to 21st century climate change across the new AR5 Earth System Models. While Northern hemisphere decreases in biomass and productivity are dramatic and consistent across all models, biomass and productivity decrease far less (or even increase) in the southern hemisphere. Based on a physical, biogeochemical and ecological analysis and informed by Lovenduski and Gruber (2007), we propose a new paradigm for the Southern Ocean ecological response to climate change. The Southern Ocean is divided in frontal bands, defined by increases or decreases in productivity. We study how these banded structures are driven by changes in temperature, light limitation and nutrient limitation. The southward shift in the subtropical-subpolar boundary modifies the nutrient and phytoplankton behavior at 40°S-45°S. The expansion of the subtropics favors increased convergence of heat at the subpolar-subtropical boundary and increased temperature-driven phytoplankton growth. The intensification of mid-latitude westerlies associated with an increasing SAM changes the patterns of circulation and mixing in the Southern Ocean affecting upwelling strength, mixed layer depth and hence light and nutrient limitation differentially across different latitude bands. The seasonal, interannual and interdecadal variability of the Southern Ocean ecology are also discussed.

**Marine aerosol and its possible contribution to the changing westerly winds**

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Model estimates of mass distribution and composition of organics injected from the sea to the atmosphere have been linked to chlorophyll in the upper mixed layer, wind speed and wave breaking. We adapt an existing biogeochemistry model by adding the following: Polysaccharides, protein, lipids and humics to simulated values of the dissolved organic matter (DOM). DOM distributions are estimated from the Biogeochemical Elemental Cycling Model ecosystem dynamics package [Doney et al., 2001; Wang and Moore, 2011], a standard component of Parallel Ocean Program, which is part of the Community Earth System Model.

Organic macromolecules are important because they form a film on the sea surface which inhibits air-sea transfer of climate gases including CO₂ and dimethylsulfide (DMS) [Liss and Duce, 1997; Leifer and Patro, 2002]. Some of the key organics are polysaccharides, protein and lipids. These molecules can be aerosolized by wind-driven bubble breaking and contribute significantly to global radiative forcing by modulating cloud brightness through the distribution of cloud condensation nuclei. A global contribution of 30 (19-37) Tg S yr⁻¹ from DMS was estimated for the years 2000-2009 and the climatological average for 1978-2008 is 28.1 (17.6-34.4) Tg S yr⁻¹ [Wingenter et al., in prep.; Lana et al., 2011]. Some of the sulfur will form secondary aerosols after oxidation. The flux of
marine primary organic aerosols (POA) is 40 Tg C yr\(^{-1}\) with other estimates ranging from 2-100 Tg C yr\(^{-1}\) [Long et al., 2011; Gantt and Meskhidze, 2011], which is roughly comparable to the natural sulfur flux.

We hypothesize that organic aerosols, DMS and DMS oxidation products around the Southern Ocean and coastal Antarctica are accumulating southward because of the poleward shift of the westerly winds and the intensification of wind speed. This may be feeding back positively causing the increase in reflectivity [Wingenter et al., in prep], thus further changing the westerlies. Interpretations of model output suggest the changing winds are shifting the macromolecules distribution in the ocean surface layer further eastward and southward, away from their sources, while causing homogenous concentrations in the upper mixed layer (this work).

In the summer, concentrations of polysaccharides and proteins were compared to lipids in the Southern Ocean and around the Weddell Sea. It was found that polysaccharides and proteins were a factor of ten and three higher than lipids in the upper mixed layer. However, a submicron sea spray aerosol organic mass fraction of 0.5 was estimated for the lipids around the Weddell Sea in summer as compared to 0.02 and 0.002 for protein and polysaccharides, respectively. Lipids are hydrophobic and so are predicted to be more strongly enriched at the air-sea interface and in the aerosol than polysaccharides and proteins. [Elliott et al., in prep.; Burrows et al., in prep.]

**Use of a simplified analytical model to estimate potential new production (PNP) for the waters off the Western Antarctic Peninsula (WAP) region**

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Potential new production (PNP) can be used as an adequate proxy for new primary production (nPP) and sets the upper bound limit of nitrate-derived primary production (PP). For this study, we estimate PNP by employing a one-dimensional analytical model using in situ and model data for the waters off the western Antarctica Peninsula (WAP) region for mid summer, centered around January. Field observations were made during the Palmer Long Term Ecological Research (Palmer LTER) program. A decade long time-series of NO\(_3\) vertical profile data (1998-2007, N=516) was used for PNP computations.

PNP was calculated for the WAP region by subdividing it into three sub-regions i.e. coastal, shelf and slope based on bathymetry and water mass properties. The coastal sub-region includes waters with bathymetric depths of 450m or less with slope water accounting for the oceanic region greater than 750m water depth, while the extensive shelf region occupies the area between these depth limits. Mean PNP estimates were computed to be 2482.6 ± 197.5, 384.5 ± 61.7, and 891.1 ± 81.8 mg C m\(^{-2}\) d\(^{-1}\) for the
coastal, shelf and slope sub-regions, respectively. The estimated overall mean PNP rate for the entire Palmer LTER WAP region during mid summer was $1257.5 \pm 113.6 \text{ mg C m}^{-2} \text{ d}^{-1}$. The mean potential f-ratio (PNP:PP) for the WAP region was closer to unity (potential f-ratio = 1.2) indicating that nPP (as opposed to recycled production) played a major role in sustaining this sporadic but highly productive Antarctic ecosystem during mid-summer. We have also analyzed a longer time series from oceanic sampling stations off Palmer Station, Anvers Island, Antarctica spanning year-days 310-45 (late November – mid February, 1994-2007). Harmonic regression fit of PNP data from all stations within this finer sampling grid of the Palmer LTER Program during the growth season provides maximum and minimum PNP rates of 2181.78 and 14.69 mg C m$^{-2}$ d$^{-1}$ on year-days 335 (late November) and 43 (mid February), respectively. The overall mean PNP for this region was estimated to be $1040.93 \pm 764.58 \text{ mg C m}^{-2} \text{ d}^{-1}$ by employing a constant $K_z$ value of $10^{-5} \text{ m s}^{-2}$. The minimum and maximum PNP values coincide approximately with the onset and demise of bloom conditions.

Analyses of the terms used in the PNP equation indicate that both NO$_3$ drawdown rates (mean= $13.25 \pm 9.57 \text{ mmol m}^{-2} \text{ d}^{-1}$, N=156) and NO$_3$ flux into the euphotic layer (mean = $1.36 \pm 1.79 \text{ mmol m}^{-2} \text{ d}^{-1}$, N = 156) have high temporal and spatial variability. NO$_3$ drawdown rates were higher than NO$_3$ flux into the control volume by approximately an order of magnitude. Sensitivity analyses of the model using two extreme values of $K_z$ ($10^{-4}$ and $10^{-5} \text{ m s}^{-2}$) that are widely reported in the literature for the WAP region, yielded a PNP difference of 97.13 mg C m$^{-2}$ d$^{-1}$. The latter accounted for approximately 10% of the overall computed PNP. PNP estimates for the coastal sub-region which includes Marguerite Bay, agreed well with estimates of nPP from north Marguerite Bay in a recent study which employed different datasets and research approach.

**NPZD-iron lower level ecosystem model of the Ross Sea**

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The Ross Sea continental shelf is the single most productive area in the Southern Ocean, and may comprise a significant but unaccounted for oceanic CO$_2$ sink, largely driven by phytoplankton production. However, the processes that control the magnitude of primary production in this region are not well understood. During summer, an observed abundance of macronutrients and scarcity of dissolved iron are consistent with iron limitation of phytoplankton growth in the Ross Sea polynya, as is further suggested by shipboard bioassay experiments. Field observations and model simulations indicate four potential sources of dissolved iron to surface waters of the Ross Sea: (1) circumpolar deep water intruding from the shelf edge; (2) sediments on shallow banks and nearshore areas; (3) melting sea ice around the perimeter of the polynya; and (4) glacial meltwater from the Ross Ice Shelf. These potential iron sources are isolated, either laterally or vertically, from the surface waters of the Ross Sea for much of the growing season. We hypothesize that hydrodynamic transport via mesoscale currents, fronts, and eddies
facilitate the supply of dissolved iron from these four sources to the surface waters of the Ross Sea polynya.

We propose to test this hypothesis through a combination of in situ observations and numerical modeling, complemented by satellite remote sensing. We have embedded a simple nutrient model into an idealized Antarctic coastal circulation model. This formulation includes explicit dynamics for iron, and a single phytoplankton functional group. The parameterizations used for primary production are revised to reflect physiological responses of Ross Sea phytoplankton communities. Preliminary simulation results suggest that phytoplankton growth is mainly controlled by light related to sea ice coverage and dissolved iron availability. A smaller value of nitrate uptake rate is needed to reproduce fast growth of phytoplankton during the Antarctic spring season than in Arctic region. We also found that the two major sources of iron come from the circumpolar deep water and mixing of sediments on shallow banks. We are now modifying functional groups representations to include *Phaeocystis antarctica* and diatoms, two groups of zooplankton and detritus to better represent the lower level ecosystem of the Ross Sea.

**Session 5. General**

**Carbon management in the post-Cap-and-Trade carbon economy: An economic model for limiting climate change by managing anthropogenic carbon flux**

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This abstract outlines an economic model that integrates carbon externalities seamlessly into the national and international economies. The model incorporates a broad carbon metric used to value all carbon in the biosphere, as well as all transnational commerce. The model minimizes the cost associated with carbon management, and allows for the variation in carbon avidity between jurisdictions. When implemented over time, the model reduces the deadweight loss while minimizing social cost, thus maximizing the marginal social benefit commonly associated with Pigouvian taxes.

Once implemented, the model provides a comprehensive economic construct for governments, industry, and consumers to efficiently weigh the cost of carbon, and effectively participate in helping to reduce their direct and indirect use of carbon, while allowing individual jurisdictions to decide their own carbon value, without the need for explicit, express agreement of all countries. The model uses no credits, requires no caps, and matches climate changing behavior to costs.

Along with the model, four new concepts are introduced including Carbon Quality, Carbon Toll, Carbon Morphology, and Carbon Avidity. The steps to implement the model for a particular jurisdiction are:

- Define the Carbon Metric to value changes in Carbon Quality
• Apply the Carbon Metric to assess the Carbon Toll for all changes in Carbon Quality
• Apply the Carbon Metric to assess the Carbon Morphology for imports and exports

This economic model has three clear advantages. First, the carbon pricing and cost scheme use existing and generally accepted accounting methodologies to ensure the veracity and verifiability of carbon management efforts with minimal effort and expense using standard auditing protocols. Implementing this economic model will not require any new, special, unique, or additional training, tools, or systems for any entity to achieve their minimum carbon target goals within their jurisdictional framework.

Second, given the wide spectrum of carbon affinities across jurisdictions worldwide, the economic model recognizes and provides for flexible carbon pricing regimes, but does not undermine or penalize domestic carbon-consuming producers subject to imports from exporters in lower carbon-pricing jurisdictions. Thus, the economic model avoids a key shortcoming of cap-and-trade carbon pricing, and eliminates any incentive to inefficiently shift carbon consumption to jurisdictions with lower carbon tolls.

Third, the economic model is a comprehensive, efficient, and effective strategy that allows for the implementation of a carbon-pricing structure without the complete, explicit agreement of carbon consumers worldwide.

Missing from the model is a methodology to value all aquatic carbon, including carbon in the oceans, lakes, rivers, streams, tributaries, etc. My goal at this workshop is to learn how best to extend the Carbon Metric to include all forms of aqueous carbon.

The combined effect of ocean acidification and eutrophication on water pH and aragonite saturation in the northern Gulf of Mexico

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Rising atmospheric carbon dioxide (CO₂) concentrations are increasing the amount of anthropogenic CO₂ accumulating in the ocean, and thereby acidifying ocean water. However, accumulation of anthropogenic CO₂ is not the only process affecting coastal waters. Anthropogenic inputs of nutrients to coastal waters can result in massive algal blooms, a process known as eutrophication. Microbial consumption of this organic matter depletes bottom waters of oxygen and increases their acidity through the release of CO₂. Through this study, we assess the synergistic effect of ocean acidification and eutrophication in the coastal ocean using data from six cruises in the northern Gulf of Mexico. The effect of alkalinity on coastal pH and aragonite saturation states is also investigated.
Results from a model simulation using data collected during this study indicates that eutrophication is contributing to acidification of subsurface waters and plays a larger role than acidification from atmospheric CO$_2$ uptake. Furthermore, results from the model simulation show that the decrease in pH since the industrial era is 0.05 units greater than expected from ocean acidification and eutrophication combined. The additional decrease was attributed to the reduced buffering capacity of the region and may be related to the uptake of atmospheric CO$_2$ into O$_2$-depleted and CO$_2$-enriched waters, the addition of atmospheric CO$_2$ into O$_2$-rich and CO$_2$-poor waters, the input of CO$_2$ via respiration into waters in equilibrium with high atmospheric CO$_2$, or a combination of all three processes.

**Biophysical interaction associated with the cross-shelf transport of the Mississippi River Plume**

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The Northern Gulf of Mexico is a complex marine system subject to episodic physical phenomena such as loop current eddies. Flow fields generated by these eddies can result in cross-shelf exchanges between riverine influenced shelf waters and the offshore water column. To determine the ecological effects of such exchanges, a regional 2007 cross-shelf exchange event was investigated using remotely sensed observations. Comparison of sea surface height anomaly (SSHA) observations with ocean-color products (chlorophyll-a (CHL), fluorescence line height (FLH) and colored dissolved organic matter (CDOM)) revealed elevated bio-optical signals during the exchange event associated with a counter-rotating eddy system. Here, the variation of bio-optical composition with distance to shore along the path of the exchange event is presented. The offshore ratio of bio-optical signals observed during the exchange event implies a divergence in surface water composition from the typical composition. To explore the impact of this composition change on the regional carbon budget, net primary productivity (NPP) estimates during the exchange event are compared with the climatological estimates, revealing increases of up to 330% for the corresponding time period.

**The Western Channel Observatory: A platform for carbon chemistry**

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The western English Channel is a boundary region between open shelf and coastal waters. It straddles biogeographical provinces with both boreal / cold temperate and warm temperate organisms being present and there has been considerable fluctuation of
flora and fauna since records began (Southward et al., 2005). The Western Channel Observatory (WCO) comprises of some of the longest marine time-series in the world (1903- ) and encompasses the breadth of ecosystem measurands from “photons to fish”. These data contribute to a wealth of applications, ranging from policy through technological development to pure scientific research. The WCO primary stations are at L4 (50° 15’ N, 4° 13.02’ W) and E1 (50° 2.6’N, 4° 22.5’W). These are sampled weekly and fortnightly respectively by the research vessels of the Plymouth Marine Laboratory and the Marine Biological Association. High-frequency (hourly) measurements of surface parameters are made by autonomous moorings situated at L4 and E1. These measurements have been augmented in the past decade by measurements of the various elements of the carbon system.

**Photooxidation of dimethylsulfide (DMS) in the Canadian Arctic**

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Photolysis of dimethylsulfide (DMS), a secondary photochemical process mediated by chromophoric dissolved organic matter (CDOM), has previously been demonstrated to be an important loss term of DMS in the surface layer of warm seas and the Southern Ocean. However, the role of photolysis in regulating the DMS dynamics still remains much obscure in the Arctic Ocean. This study for the first time determined the apparent quantum yield (AQY) spectra of DMS photooxidation in northern polar marine milieus covering the Baffin Bay in the eastern Canadian Arctic and the Mackenzie River estuary, Mackenzie Shelf and Canada Basin in the western Canadian Arctic. The DMS AQY was fairly invariant at salinities < 25 but rose rapidly with further increasing salinity, which is well defined by a three-parameter exponential form. Salinity can therefore be used as a quantitative indicator of the DMS AQY. The DMS AQY in the ultraviolet (UV) wavelengths was linearly and positively correlated with the spectral slope coefficient (275−295 nm) of the CDOM absorption spectrum, suggesting that marine CDOM photosensitizes the degradation of DMS more efficiently than does terrestrial CDOM. High concentrations of nitrate (~12 µmol L⁻¹) in deep water samples boosted DMS photooxidation by 70−80%, due likely to radical chemistry of nitrate photolysis. Coupled optical-photochemical modeling, based on the obtained DMS AQY spectra, shows that UV-A (320−400 nm) accounted for 60−75% of the DMS photolysis in the sunlit surface layer and that photochemistry degraded DMS on an e-folding time from 9 to 100 d (mean: 29 d). The photooxidation term on average accounted for 21% of the DMS gross
loss rate and was comparable to the atmospheric DMS ventilation rate estimated for the same geographic regions. Our finding might have wider interest and could provide results of global significance since the use of the relationship between CDOM quality/origin and AQYs maybe extended to the photochemical cycling of other compounds than DMS.