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POSTER ABSTRACTS

Better practices for management of ocean biogeochemistry data

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In anticipation of the changes expected to be made in Fall 2010 to the NSF Data Reporting Policy, staff members from the Biological and Chemical Oceanography Data Management Office (BCO-DMO) have prepared some guidelines for the two-page data management plan that will be required with every NSF proposal. The guidelines are general enough to be used with any NSF OCE proposal and we will demonstrate how following better data management practices early in a cruise-based project can facilitate data access in subsequent phases of the project. The aim is to make contribution of data and metadata as easy as possible. For ocean research cruises, a minimum of four products are recommended to document a cruise: the basic cruise metadata including a unique cruise identifier; the cruise operations report including science party manifest and data inventory; the scientific sampling event log; and the navigation data (to generate the cruise track plot). The metadata that accompany data sets managed by the BCO-DMO provide the supporting documentation describing the 'who, what, where, when, how, and why' of research cruises. The metadata records are used to power the BCO-DMO database interfaces to improve access to the data sets and to ensure accurate use of those data in collaborative research. Because it is impossible to resample environmental data, proper management of those data sets is especially important to realize the full potential of the investment of federal agency funds and to enable the synthesis of time-series collections.

Ocean biogeochemistry and marine ecosystem research projects are inherently interdisciplinary and benefit from improved access to well-documented data. In addition to supporting the OCB research community, one of the goals of the BCO-DMO is to facilitate regional, national, and international data and information exchange. Improved data sharing practices are important to the continued exploration of the research themes that are central to the OCB community, and are essential to interdisciplinary and international collaborations that address complex, global research themes.

PLENARY SESSION 1. THE ARCTIC

Freshwater and carbon dynamics in Hudson Bay

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Water mass characteristics and circulation in Hudson Bay are strongly influenced by freshwater dynamics, namely, fluvial input from the large drainage basin and sea ice formation/melt. Changing freshwater dynamics are considered to play an important role in the carbon cycle in Hudson Bay. The distribution of freshwater from different sources affects ocean chemistry, which in turn affects the saturation state of seawater with respect to calcium carbonate.

Annual time series studies have been conducted in the Hudson Bay Complex during 2003-2006, measuring dissolved inorganic carbon (DIC), total alkalinity (TA) and oxygen isotope composition ($\delta^{18}O$). Oxygen isotope composition is used to identify freshwater sources including sea ice melt water and meteoric water (precipitation and river runoff). From DIC and TA data, pH, pCO_2 and the saturation state of seawater with respect to calcite (Ω_{cal}) and aragonite (Ω_{arg}) were calculated. Highest DIC concentrations were observed at the eastern side of Hudson Bay bottom water due to a large component of brine rejection water. pCO_2 in the surface layer exceeded atmospheric equilibrium indicating that Hudson Bay serves as a source for atmospheric CO_2 during summer (August). The saturation horizon for aragonite was very shallow, less than 50 m deep, at the western side of section. Freshwater composition (sea ice meltwater vs. river water) strongly influences the saturation state in Hudson Bay.

Are phytoplankton blooms occurring earlier in the Arctic?

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Time series of satellite-derived surface chlorophyll-a concentration (*Chl*) in 1997-2009 were used to examine for trends in the timing of the annual phytoplankton bloom maximum. Significant trends towards earlier phytoplankton blooms were detected in about 11% of the area of the Arctic Ocean where data were available, e.g. in the Hudson Bay, Foxe Basin, Baffin Sea, off the coasts of Greenland, and in the Kara Sea. These areas roughly coincide with areas where ice concentration has decreased in early summer (June), thus making the earlier blooms possible. The change towards significantly earlier phytoplankton blooms may have consequences for the Arctic food chain and carbon

cycling. Outside the Arctic the annual *Chl* maximum has become earlier in boreal North Pacific but later in the North Atlantic.

Decadal trends in subpolar North Atlantic carbon uptake: Steady sink, changing mechanisms

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On the mean, the subpolar North Atlantic is the most intense carbon sink per unit area in the global oceans (Takahashi et al. 2009). Recently modeling (Ullman et al. 2009; Thomas et al. 2008) and observational studies (Schuster et al. 2009) suggest links to the North Atlantic Oscillation, but do not agree as to the direction of trends or causal mechanisms. We use a regional model to evaluate methodologies for determining trends from observations, both along the SURATLANT line (Iceland – Newfoundland, Corbiere et al. 2007) and in the Takahashi database (Takahashi et al. 2009). Using a robust methodology, we find that the subpolar North Atlantic pCO_2 trend is not significantly different from the atmospheric trend, i.e. there has been a steady sink, for the past 3 decades. However, the mechanisms responsible for this steady uptake have changed. From 1993-2005, warming SSTs were primarily responsible for the increasing pCO_2 in the subpolar gyre, with minimal trends in the non-temperature component. SURATLANT data suggest that this occurs because the effect of accumulated dissolved inorganic carbon was counteracted by a simultaneous increase in alkalinity. In contrast to the temperature driven trends for 1993-2005, we find for 1981-2009 that the subpolar pCO_2 trend is driven by the non-temperature component. Decadal-timescale shifts in subpolar surface fluxes and circulation appear to substantially modify the mechanisms of carbon uptake.

Seasonality of the ecosystem response to iron stimulation in the Southern Ocean

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Mesoscale iron enrichment experiments and studies of natural iron inputs, in high nutrient low chlorophyll (HNLC) waters have demonstrated that iron limitation is widespread and affects atmospheric carbon dioxide and thus global climate. Of the HNLC regions, the Southern Ocean plays the greatest role in the global carbon cycle, but the dominant controls on net algal production are still controversial. Although broad ecosystem responses among mesoscale experiments are similar in different oceanic regions, the biomass generated and carbon dioxide drawdown at the surface differ substantially. Here we apply a lower trophic level Nitrate-Phytoplankton-Zooplankton-Detritus (NPZD) ecosystem model to investigate the effect of iron on phytoplankton

growth in response to different iron-enrichment simulations in the Australasian-Pacific sector of the Southern Ocean. While the ecosystem model represents a simple approximation of the complex lower trophic ecosystem of this region, simulated chlorophyll concentrations reproduce the main characteristics of the first Southern Ocean Iron Release Experiment (SOIREE), the surrounding HNLC environment, and the naturally iron fertilized waters of the Kerguelen plateau. Furthers runs with the same iron enhancement treatment differed dramatically according to the different location and time of the year of the simulated iron infusions. The magnitude of the iron-induced biogeochemical responses in surface waters, such as maximum chlorophyll, is strongly controlled by both light and grazing pressure, and shows highest values during the early spring infusions. In contrast, the highest POC export estimates are observed during the summer infusions. These findings suggest that not only light limitation but also the overwintering biomass of phytoplankton and their principle grazers are crucial factors in the response of phytoplankton community to iron enrichment.

Effect of environmental variables on eukaryotic microbial community structure of land-fast Arctic sea ice

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Changes in sea ice community structure affect carbon and nutrient cycling in polar seas, but the response in microbial species composition to key environmental variables still remains largely descriptive. Using ice cores recovered from 3 locations near Point Barrow, AK in May 2006, we document the diversity and composition of eukaryotic sea ice microorganisms in relation to vertical depth within the cores, light availability (mainly as variable snow cover) and nutrient concentrations. We used DGGE (denaturing gradient gel electrophoresis) of a PCR (polymerase chain reaction) amplified section of the 18S rRNA gene in combination with epifluorescence microscopy to compare the community structure of the major eukaryotic microbial phylotypes in the ice. We find that the community composition of the sea ice is more affected by the depth horizon in the ice than by light availability, although there are significant differences in the abundance of some groups between light regimes. This underscores the importance of snowfall and snow distribution for sea ice microbial community structure on scales of only meters, and the potential impact of climate change on sea ice ecosystems. Epifluorescence microscopy shows a shift from predominantly heterotrophic life styles in the upper ice to autotrophy prevailing in the bottom ice. Clone libraries constructed using diatom specific primers confirm the high diversity of diatoms in the sea ice, and support the microscopic counts. Evidence of protistan grazing upon diatoms was also found in lower sections of the core, with implications for carbon and nutrient recycling in the ice.

Spring primary production on the eastern Bering Sea Shelf as estimated from oxygen/argon ratios and triple oxygen isotopes

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The eastern shelf of the Bering Sea is the most productive U.S. fishery. Changes in the Bering Sea ecosystem observed in recent decades have been correlated with climatically induced changes in regional environment. However, specific mechanisms underlying the observed correlation are not known, and require a better understanding of the multiple factors influencing the magnitude of primary production in the region.

Here we report estimates of Net Community and Gross Photosynthetic Production rates (NCP and GPP) obtained from $[O_2]$, O_2/Ar and triple oxygen isotope ratios measured as a part of the BEST (Bering Sea Ecosystem Study) project in spring of 2007 and 2008. The data were obtained by continuous underway measurements with an optode and EIMS (Equilibrator Inlet Mass Spectrometer), plumbed into the ship, USCG Healy, seawater underway system. GPP rates were calculated from ^{17}O excess measured on discrete samples collected from the mixed layer through the duration of both cruises.

The 2007 cruise track intersected intensively blooming fields associated with the retreating ice edge. Using piston velocities from Quikscat wind speeds, rates of NCP in the ice-edge blooms were calculated with the assumption of steady state. In spring 2007, the NCP-O_2 rates within the bloom ranged from 500 to over 1000 mmol m^{-2} d^{-1}, and NCP/GPP ratios in the bloom approached 80%. Rates of NCP measured in the spring season of 2008 were lower, up to 500 mmol m^{-2} d^{-1} and NCP/GPP ratio did not exceed 60%. We present a time-dependent model simulating gross and net production in the mixed layer, and compare the productivity rates calculated using the steady state assumption with the modeled rates with incorporation of the bloom dynamic. Using the model, we evaluate factors, which determine the rates of NCP and GPP during spring season on the Bering Sea Shelf.

Effect of ocean acidification on the speciation of metals

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Burning of fossil fuels and other human activities has caused the atmospheric concentration of CO_2 to increase. Oceanic uptake of a portion of this CO_2 has led to a decrease in ocean pH from 8.2 to 8.1 since preindustrial times. A decrease to 7.4 is predicted under business as usual scenarios. This leads to a decrease in $[OH^-]$ and $[CO_3^{2-}]$. Most studies of the impacts of this acidification focus on calcifying organisms due to the lowering of $CaCO_3$ saturation states, but until recently only a few studies have

considered potential impacts on other organisms, ecosystems, and ocean chemistry. Besides lowering the CO_3^{2-} concentration, the decrease in pH will change the organic and inorganic speciation of trace metals in seawater. These changes will influence metal interactions with marine organisms as well as kinetic and equilibrium processes. Changes in speciation will affect solubility, adsorption, toxicity, bioavailability, and rates of redox processes. Using published stability constants (β) and the Pitzer ionic interaction model we predict speciation changes for most trace metals in seawater. We predict iron solubility and bioavailability to increase and copper toxicity to also increase. Such changes could influence primary productivity and biogeochemical cycling.

PLENARY SESSION 2. LOW-OXYGEN REGIONS

Twists in estimating temporal O_2 changes in oxygen minimum zones from old O_2 data

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Are the three major open-sea oxygen minimum zones (OMZs) currently intensifying and expanding? Accurate time series are required for the answer. Our poster concerns changes in accuracy of O_2 data since the end of the IGY (1958/59). While electrodes now routinely measure O_2 in the water column, calibration through Winkler titration of water samples is still needed. The end point of the titration used to be detected visually by adding starch as an indicator (VED herein). In the last two to three decades automated photometric, potentiometric, or amperometric approaches (AED, for automatic) has become the norm, although VED is still used occasionally. The poster points out and illustrates that the VED yields O_2 values higher than the AED by 0.05 up to 0.10 mL L^{-1} (~2-5 μM), a large amount relative to the ambient O_2 concentrations in OMZs, which can be close to zero micromoles.

Oceanographic data centers, e.g., the U.S. NODC, have not yet recognized the systematic error (bias), but have only removed variability (outliers, duplicates, etc.) by statistical analysis. The early O_2-values are not flagged. Therefore, when O_2 time series at very low O_2 concentrations are extended back to 1960, bias in the VED observations from the 1960s onward may falsely make a decadal decline of O_2 appear as real.

The bias in the VED data will vary and there is no good general remedy because the operator errors cannot be assessed post hoc. So investigators looking into time series of O_2 in OMZs need to forego the use of averages and interpolations, as they are the basis for climatologies or the World Ocean atlases issued by NOAA, and pursue the original data and methods. Errors may not only arise from incorrect end point detection but may

be caused by insufficient flushing when filling the O_2 bottles. An additional source of error may be NO_2^-, which appears when O_2 falls below 1-2 μM due to reduction of NO_3^-. Catalytic oxidation of iodide to I_2 by NO_2^- after acidification of the Winkler samples generates apparent O_2. The NO_2^--interference is eliminated by azide added to the KI-NaOH reagent. We currently study the issue of correction of the small error from NO_2^-. Records from AED analyses with O_2 clearly higher than 1-2 μM and with NO_2^- in the same samples above the error of analysis of, say, 0.2 μM NO_2^- are likely to be erroneous and may be removed.

Is the now recurrent anoxia of the SW monsoon off India's west coast to last?

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During the southwest (summer) monsoon season, cool mid-thermocline water is upsloping all along India's and Pakistan's Arabian Sea shelves. Remotely driven Kelvin waves and more local winds may cause actual upwelling to the surface. Overall, the region during this season is similar to an eastern boundary current but under heavy rain. Water of about 0.5-1.0 mL L^{-1} O_2 (10-20% of saturation) is present for 4-5 months on the shelf. The resulting phytoplankton blooms ultimately not only cause the large catches of pelagic fish but below the shallow thermocline also a high O_2 demand. Through at least the 1980s near-bottom water O_2 content seems to have been quite low but not anoxic (sulfidic). After about the mid 1990s, though, broad removal of sub-thermocline NO_3^- over the shelf and H_2S on the inner shelf have been present yearly for about 2 months over about 10° of latitude, with drastic effects on the fisheries for demersal fish and prawns.

Given the low O_2 content in the advected water while on the shelf, only relatively small additional amounts of organic matter are needed to achieve anoxic conditions. It was unknown and difficult to disentangle whether the shift is due to (**A**) higher phytoplankton production from the greatly increased use of agricultural fertilizers and runoff, as well as atmospheric nitrogen deposition, or (**B**) a climate-caused hydrographic change, e.g., slightly less oxygenated source water, or increased residence time on the shelf (of which either one may revert to the earlier state), or (**C**) combinations thereof.

We find now that the additional NO_3^- from runoff and atmospheric deposition, which is "diluted" 5-10 times by originally NO_3^--rich seawater, is unlikely to remove the initial NO_3^- inventory even on the inner shelf (~15 m depth; our choice **[A]**). It certainly is out of the question over a deeper water column. So, the cause of the recent anoxia may be

hydrographic change (choice **[B]**). Thus, the environment may at some time revert to the state observed through the 1980s.

Temporal evolution of oxygen minimum zones in a global ocean model

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The future of oxygen minimum zones is of importance to marine ecosystems and biogeochemical cycles. Here we use a global biogeochemical model hindcast from 1959-2005 to analyze temporal and spatial development of hypoxic and suboxic zones to identify processes and mechanisms leading to the creation and demise of such zones. We find the strongest oxygen variability in the depths of mode water masses, where the modeled minimum zones are also located. Our model runs show that the volume of suboxic water in the world ocean can vary on a decadal time scale by >50%, and that fluctuations in the rate of nitrate reduction by denitrification may be even larger.

Temporal variability of the physicochemical water characteristics at a coastal monitoring observatory: Station ENSENADA in Baja California, Mexico

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The physicochemical conditions of coastal waters off Ensenada, Baja California (Mexico) were characterized over time. Moreover, the physicochemical conditions at a coastal monitoring observatory, called station ENSENADA, were described using a two-year data series obtained with greater temporal sampling frequency. The historical analysis of line 100 showed marked seasonal variability in the physicochemical conditions of the coastal waters, associated with fluctuations in the flow of the equatorward California Current and poleward subsurface waters, as well as with coastal upwelling events whose magnitude and frequency increase towards spring-summer (Linacre et al., *In press*). Interannual variability was also observed, related to warm and/or cold periods that modify the characteristics of the water column in this coastal region. Seasonal variations at station ENSENADA, indicating that this site is sensitive to interannual signals such as La Niña events. The temperature, salinity, dissolved oxygen, density, and dissolved inorganic carbon data for spring 2008 revealed the anomalous presence of bottom water at the surface, associated with the 2007/2008 La Niña. The results suggest that this is a good location for monitoring the oceanographic conditions of northern Baja, California.

Phosphorus fractions within Louisiana Shelf sediments and their diffusive flux response to water column anoxia

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Anthropogenic nutrient loads to the Louisiana Shelf have drastically increased since the mid 1900s. Though the main nutrient delivery mechanism in this region is well understood to originate from riverine sources, great uncertainty still remains regarding the contribution of sediment nutrient regeneration and submarine groundwater discharge to primary production within the shelf and adjacent regions. In this study we report results from laboratory manipulations of surface sediments and intact sediment cores collected along seven different locations within the Louisiana Shelf between June 27th - July 5th, 2009. Chemical fractionation of surface sediments indicates that a non-insignificant fraction of the sedimentary phosphorus pool is bound to the reducible fraction (citrate-dithionate buffer), presumably as oxides or oxyhydroxides of iron. Results from triplicate intact core laboratory incubations under both oxic and anoxic water column conditions show a significant increase in diffusive phosphorus flux from sediment to overlying water column under anoxic conditions. Mean diffusive phosphorus flux from sediments under oxic conditions ranged between 5.51 and 118, whereas mean anoxic phosphorus flux during the initial (t = 0 to 1day) and long term (t = 1 to 14 days) phases of the incubations ranged between -100 and 608, and -33 and 83 μmol P/m^2/day, respectively. Our data indicate that bottom water anoxia represents a significant mechanism leading to the release of phosphorus from sediments within the Louisiana Shelf region. Increased bottom water shear (wind- or wave-driven) during periods of anoxia could lead to significant further translocation of phosphorus to the water column. Preliminary analysis of our results indicates that during peak summer months (June-August) diffusive sedimentary inorganic phosphorous loads to the shelf induced by anoxia are of comparable magnitude to riverine Ortho-P loads. Our results emphasize the importance of including sedimentary processes within coastal zone nutrient budgets of this region.

Acidification of northern Gulf of Mexico continental shelf bottom waters caused by hypoxia

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Four cruises were carried out in 2009 to investigate the seasonal carbon cycle in northern Gulf of Mexico shelf waters, which are subject to both freshwater input from rivers (e.g.,

Mississippi, Atchafalaya) and summertime hypoxic stresses. In our summer cruise, hypoxic bottom waters were observed off the Louisiana coast. This hypoxic condition corresponded to elevated dissolved inorganic carbon (DIC) concentrations (up to ~2280 μmol/kg) and pCO_2 (>1100 μatm), along with depressed pH as low as ~7.7, compared to DIC of ~2100-2150 μmol/kg, pCO_2 of 450-500 μatm, and pH>7.9 in adjacent non-hypoxic bottom waters. As a result of the buildup of respiration products, carbonate saturation state decreased to less than two times the aragonite saturation ($\Omega<2$), as compared to $\Omega>3$ in non-hypoxic bottom waters. On the other hand, the water column in all other seasons (spring, fall, and winter) was relatively well mixed except in areas directly affected by river flumes. Summertime stratification and bottom water respiration following enhanced springtime primary production are believed to cause bottom water hypoxia, which in turn leads to enhanced acidification in the stagnant bottom waters. This type of seasonal acidification in hypoxic-prone coastal seas is much stronger than that in the open ocean, the latter being caused by anthropogenic CO_2 intrusion. However, future increases in atmospheric CO_2, enhanced nutrient input from agriculture usage, and continuing wetland loss due to sea level rise may further exacerbate this problem.

Climate and larval fish assemblages in the Southern California Current, 1951–2008

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Principal component analysis (PCA) was used to analyze temporal patterns in abundance of 86 common taxa of larval fishes that have been consistently identified since 1951 as part of the California Cooperative Fisheries Investigations (CalCOFI) program. The first three PCs explained 20.5, 12.4 and 6.8% of the variance of the data set (total: 39.7%). each was associated with distinct assemblages: PC 1 with the mesopelagic fauna, PC 2 with epipelagic and shallow-water fishes, and PC 3 with reef and coastal fishes. Despite the ecological and taxonomic diversity of the data set, fully 48 of the 86 ichthyoplankton taxa were significantly positively correlated with PC 1 and only three negatively with it, indicating a broad community response to regional environmental forcing. Of the 25 taxa correlated with PC 1 at a level of 0.5 or greater, 23 were mesopelagic fishes from a diverse range of families. PC 1 was highly correlated with decadal trends in midwater oxygen content ($\rho = 0.73$, $p < 0.001$), and was also significantly correlated with the El Niño-Southern Oscillation (ENSO) and Multivariate ENSO Index (MEI), the Pacific Decadal Oscillation (PDO), and temperature at 200 m. Oxygen at 200 m and the PDO entered a stepwise regression significantly and together explained 65% of the variance of PC 1. PCs 2 and 3 were significantly correlated with mean sea surface temperature (SST) and the North Pacific Gyre Oscillation (NPGO), respectively. These are the first reported results to indicate that the midwater fish community responds coherently to decadal changes in midwater oxygen content, as well as to the large-scale regime shifts represented by the PDO. The mesopelagic and shelf/slope demersal fish taxa that loaded

significantly on PC 1 declined on average 57% from periods of high to low oxygen concentration in the oxygen minimum zone. Our results suggest that the mesopelagic fauna is highly sensitive to changes in deepwater oxygen levels, which several climate models predict will decline in the deep ocean as a consequence of global warming.

Total inorganic carbon versus apparent oxygen utilization above and within the oxygen minimum zone in the Mexican Pacific

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In the Mexican Pacific south of the Gulf of California, the mean slope in the scatter plot of total inorganic carbon (TIC) vs. apparent oxygen minimum (AOU) between the surface and the core of the oxygen minimum zone (OMZ) was found to be 0.8 +/-0.17 in Feb. 2005 and 1.3 +/-0.15 in Nov. 2009 (molar ratio +/- 95% confidence). The following issues could possibly influence this ratio: (a) The preformed TIC in the OMZ could vary because this OMZ is formed by two water masses of different age, hence of differing atmospheric partial pressures of CO_2 at the time of submergence. (b) The TIC and AOU are in different states of atmospheric disequilibrium due to changes vertical exchange rates between the mixed surface layer and the OMZ governed by vertical stratification. (c) The respiratory quotient (RQ) for micro-aerobic regimes within the OMZ is little known. (d) The dissolving of particulate inorganic carbon (PIC) on its passage (i.e. sinking) through the OMZ can increase TIC. Preliminary interpretation suggests that (b) is the most likely reason for different TIC vs. AOU ratios found in the two cruises.

Oxygen minimum zones in the Community Climate System Model 4.0 Ocean Model

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Oxygen minimum zones are a key site of denitrification in the oceans, and may thus influence ocean productivity and climate over sufficient timescales. I will document the size and extent of oxygen minimum zones (OMZs) in the NCAR Community Climate System Model. The intensity and spatial extent of the OMZs are overestimated in this model. I will examine the sensitivity of the OMZs to modifications of several physical parameters that influence ventilation, and to several biological parameterizations that influence the flux of sinking organic matter in the OMZ regions.

Classification of phytoplankton in the South Atlantic next to the Argentinian continental shelf and its relation to hydrographic parameters

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The studied zone, in the southwestern Atlantic Ocean and over the Argentinian continental shelf (between 36º and 50ºS), represents a confluence zone located between the Malvinas and Brazil currents. This zone has a wide continental shelf with shallow and euphotic waters, very nutrient rich. For these reasons, this shelf is characterized by the proliferation of phytoplankton with areas of high biomass accumulations, and may represent an important carbon drain for this area.

Phytoplankton groups can be classified on the basis of pigment composition, determined by HPLC.

NASA classification (SeaHARRE-2, Hooker et al, 2005) yields three groups according to phytoplankton size (microphytoplankton, nanophytoplankton and picophytoplankton). But with the CHEMTAX program (Mackey, 1996), it is also possible to determine the phytoplankton functional groups or class abundances. These results can also be compared with satellite data, increasing the information that can be obtained from satellite observations.

With the determination of phytoplankton pigment composition in several oceanic stations near the Argentinian continental shelf, and the application of the NASA classification and CHEMTAX program, it is possible to evaluate spatial variability of phytoplankton dynamics in the area, and to quantify and classify different phytoplankton classes present. We also observe regional relationships between different phytoplankton populations and hydrographic conditions.

These results have been related with marine biogeochemical factors in our study area, especially those related to carbon dioxide and oxygen concentrations, and their implications for carbon and nutrient cycling.

Decadal changes in the subtropical South Pacific

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Over the past several decades, changes in the apparent oxygen utilization (AOU) and total dissolved inorganic carbon (TC) have been observed throughout the global oceans. Recent investigations in the North Pacific indicate the observed decadal change in AOU can be attributed to natural variation in ocean circulation and a significant portion of the total change in TC is attributed to AOU variability and not anthropogenic forcing. Here we present observations of the decadal variability in the South Pacific on WHP section

P06, nominally along 32°S. Unlike other sections in the region, P06 has been occupied by three global hydrographic programs: during WOCE in 1992, on the BEAGLE cruises during 2003, and most recently during the CLIVAR program in 2009/10. Variability in AOU is investigated on both neutral density surfaces and with the extended multiple-parameter linear regression technique (eMLR). The eMLR is also used to investigate changes in the anthropogenic CO_2 inventory and the subsequent changes in pH and carbonate mineral saturation horizons. Changes in the decadal variability of these parameters are investigated by making comparisons between the WOCE-CLIVAR, BEAGLE-CLIVAR, and CLIVAR-BEAGLE data sets.

SESSION 3. BENTHIC-PELAGIC INTERACTIONS

Carbon dioxide dynamics and ecosystem metabolism in the Mississippi River plume

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Dissolved inorganic carbon (DIC), total alkalinity (TAlk), pH, and dissolved oxygen (DO) were determined in the Mississippi River plume during many cruises conducted between 2004-2010. In contrast to many other large rivers, both DIC and TAlk were higher at the river end-member than in seawater during the surveys. Substantial losses of DIC, relative to TAlk, occurred within the plume, particularly at intermediate salinities. DIC removal was accompanied by high DO, high pH, and nutrient depletion, and was attributed to high phytoplankton production. Salinity and TAlk were used to delineate a complicated mixing system that involves multiple and variable river end-members. Then, net ecosystem production (NEP) rates were estimated from DIC budget. Estimated plume-average NEP peaked at 4.3 g C m^{-2} d^{-1} during summer, which is the highest reported for large river plumes studied to date. Influencing factors of saturation state of $CaCO_3$ were also discussed. In summer and fall, biological production in the turbidity plume consumed the majority of the available nutrients, while during spring only 14-17% of the available nutrients were utilized in the plume. This study is the first plume-wide productivity observation through carbonate system and the results are comparable to biological observations.

Insight into the nitrogen budget of the eastern Bering Shelf from the N and O isotope ratios of nitrate

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We present a survey of fixed N over the Bering shelf in spring, in which we exploit the stable isotopic tracers of reactive nitrogen species to investigate the N dynamics of the shelf. In April of 2007 and April of 2008, we collected samples for analysis of the stable isotope ratios of nitrate and other N species at multiple stations throughout the eastern Bering Shelf. We present measurements of the N and O isotope ratios of nitrate ($^{15}N/^{14}N$ and $^{18}O/^{16}O$, respectively), and of the $^{15}N/^{14}N$ of surface sediments at stations throughout the shelf, the distribution of which we examine in relation to a comprehensive set of ancillary hydrographic measurements. We seek to identify 1) the provenance of nitrate on the shelf, 2) the extent of fixed N loss to sedimentary denitrification and the consequent isotopic imprint on shelf N, if any, and 3) the contribution sediment remobilization to nutrient recharge of the shelf prior to the spring bloom. Our analysis reveals that the isotope ratios of nitrate in the water column are manifestly influenced by N transformations occurring in sediment, and identifies nitrification-coupled denitrification in sediment as a prominent mechanism of fixed N loss throughout the shelf. The nitrate isotope ratios also evidence that sediment processes concurrently give way to substantial remobilization of fixed N to the water column, and thus contribute significantly to seasonal nitrate recharge of the water column. Moreover, nitrification-coupled denitrification also appears to communicate sizeable ^{15}N-enrichment to reactive N in the overlying water column, communicating an N isotope effect between 4‰ and 8‰ – such that reactive N exported to the Arctic at Bering Straight is likely ^{15}N-enriched compared to surface nitrate off-shelf. These observations lead to hypotheses on the potential impacts of changing ice cover and hydrography on nutrient dynamics of the Bering shelf, and also demonstrate that N isotope tracers provide a sensitive tool that will be valuable to monitor changes in N biogeochemistry of the shelf in light of a changing climate.

A new radiocarbon measurement tool for ocean carbon cycle studies

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We have developed and interfaced a gas accepting ion source-continuous flow accelerator mass spectrometer system (GIS-CFAMS) for radiocarbon measurement. We describe the principles and characteristics of this new tool and its potential benefits and limitations for oceanographic research. This unique system has been successfully

interfaced to a gas chromatograph and we have performed GC-CFAMS radiocarbon measurements of individual compounds in complex organic mixtures. We have also coupled the system to an equivalent to a Gas Bench (R), an automated gas dispensing system with the intent of demonstrating the possibility of rapid reconnaissance radiocarbon measurements of coral samples. Recent experiments indicate that 0.6% radiocarbon measurements are possible with a ~5-minute measurement. We speculate on future possible applications for ocean carbon cycle research.

U.S. Eastern Continental Shelf Carbon Cycling (USECoS): Modeling, data assimilation, and analysis

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Although it is well understood that the oceans play a major role in the global carbon cycle, there is still much debate about the magnitudes and distributions of carbon fluxes on continental shelves. Many key shelf fluxes are not yet well quantified: the exchange of carbon across the land-ocean and shelf-slope interfaces, air-sea exchange of CO_2, burial, and biological processes including productivity. The goal of the USECoS (U.S. Eastern Continental Shelf Carbon Cycling) project is to quantify these carbon fluxes along the eastern U.S. coast using models quantitatively verified by comparison to observations, and to establish a framework for predicting how these fluxes may be modified as a result of climate and land use change. This study builds on results from our earlier NASA-funded study of carbon cycling, which resulted in development of a coupled biogeochemical-ocean circulation model configured for the U.S. eastern continental shelf.

This model was extensively evaluated with in-situ and remotely-sensed data. Results indicated that reduction in uncertainties in the shelf component of the global carbon cycle required 1) increased resolution of the physical model via nesting, 2) refinements of the biogeochemical model, and 3) quantitative evaluation of these via assimilation of biogeochemical data (in-situ and remotely-sensed). These model improvements will be described and their consequences for simulation of carbon cycling on the U.S. east coast continental shelf discussed. The resultant model provides a framework for better understanding and reducing estimates of uncertainties in current and future carbon transformations and cycling in continental shelf systems.

$CaCO_3$ dynamics in biogenic carbonate sands

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Reduced net calcification owing to increasing pCO_2 from the burning of fossil fuels suggests a potential reduction in carbonate accumulation in continental margins, where a large fraction of global carbonate accumulation occurs. These effects lend particular importance to understanding the factors controlling carbonate accumulation and dissolution in coastal and shelf deposits. Increasing attention has been focused on the biogeochemistry of permeable sands in part because of the areal significance of these sediments in continental shelves worldwide and the high metabolic activity characteristic of these deposits. As a result of the interplay between organic matter remineralization, benthic photosynthesis, carbonate dissolution and calcification in carbonate reef sands, these biogenic deposits are poised to play a crucial role in the response of ocean margin ecosystems to ocean acidification.

A new technique has been developed to measure carbonate dissolution kinetics using microsensors in permeable sediment cores, in contrast to kinetic experiments previously conducted at lower solid:solution ratios. Measurements of carbonate solubility based on batch incubations and dissolution kinetics in core percolation experiments with permeable carbonate sands will be discussed. Laboratory kinetic and solubility measurements will also be applied to interpret measured benthic fluxes (Ca^{2+}, pH, Alk, DIC, O_2), porewater profiles, and sediment oxygen consumption rates in reef sands on Heron Island, Australia.

Deep-ocean observatories in Europe

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The European Seas Observatory NETwork Network of Excellence (ESONET NoE) and EuroSITES programmes aim to increase our understanding of the deep-sea and its coupling to the surface ocean and climate, as well as marine geo-hazards. Substantial efforts are now underway to realise an urgently needed organization to operate deep-sea observatories around European Seas including the European large-scale research Infrastructure programme EMSO (European Multidisciplinary Seafloor Observatory). The needs for a network of ocean observing systems cross many areas of earth and marine science. Understanding from existing studies is fragmented because it lacks the coherent long-term monitoring needed to address questions at the scales essential to understanding climate change and improve geo-hazard early warning. Data from the deep sea are particularly rare with long-term data available from only a few locations, the

longest of which extend back about three decades. These science areas nonetheless have impacts on societal wellbeing. There is now wide recognition that research addressing science questions of international priority, such as understanding of the potential impacts of climate change or geo-hazards like earthquakes and tsunamis should be conducted in a framework that can address questions across adequate temporal and spatial scales. The development of ocean observatories provides a substantial opportunity for ocean science to evolve in Europe. Active research using observatories in EuroSITES is beginning to provide standardized data capable of bridging various measurement scales across a dispersed network in European Seas. Similarly future observatory science and technical planning are progressing in ESONET and plans to create of a legal organisation to operate European deep-ocean observatories are progressing in EMSO. The connection of ocean observatory research into larger frameworks including the Global Earth Observation System of Systems (GEOSS) and the Global Monitoring of Environment and Security (GMES) programme is integral to success. It is in a greater integrated framework that the full potential of the component systems will be realised.

Fluorescence characterization of organic matter released from Piraeus Port sediments

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Piraeus port is located at the crossroads of three continents, Europe, Africa and Asia. It has been the port of Athens for more than 2500 years. It is the largest Greek seaport, one of the largest seaports in the Mediterranean Sea basin, the third most frequented passenger port in the world, the largest passenger port in Europe, one of the top ten container ports in Europe and the leading container hub in the Eastern Mediterranean. The main port areas are a central passenger port, a container terminal, a cargo terminal, an automobile terminal, and a ship repair and maintenance site.

The present work involves the evaluation of the fluorescence spectra of dissolved organic matter (DOM) aqueous extracts isolated from four sediment samples collected by a grab from Piraeus Port in May 2009. DOM plays an important role in interacting with a wide range of pollutants, mainly by enhancing bioavailability, thus causing an increased toxicity for some pollutants, while allowing the relatively insoluble pollutants to be metabolised. Further, DOM may affect the co-transportation of pollutants to the soluble phase.

Samples were collected from four sites: Two located in the outer harbor close to the coastline at 10 m water depth; the third located between Psitalia Island, location of the Wastewater Treatment Plant of Athens, and the northeastward coastline at 35 m water depth; and the fourth located seaward of the outer cargo terminal at 27-m water depth. All samples were analyzed for total organic carbon (TOC) content, which was found to be between 11.3 and 11.7 mg L^{-1}.

DOM was extracted under gentle extraction conditions (4 mM $CaCl_2$ solution) and characterized by applying the rapid, sensitive, non-destructive method of fluorescence spectroscopy, in an attempt to distinguish different classes of organic components.

Fluorescence spectra were recorded using a Perkin-Elmer LS 55 luminescence spectrophotometer equipped with the WinLab 4.00.02 software for data processing. Mono dimensional emission spectra were recorded over the range 380–600 nm at a constant excitation wavelength of 360 nm. Excitation spectra were recorded over the range 300–500 nm at a fixed emission wavelength of 520 nm. Synchronous-scan excitation spectra were measured by scanning simultaneously both the excitation and the emission wavelengths (from 300 to 550 nm), while maintaining a constant, optimised wavelength difference $\Delta\lambda$ (λem – λexc) = 18 nm. (Senesi et al., 1991). Total Luminescence Spectra were obtained in the form of excitation/emission matrix spectra (or contour maps) by scanning the wavelength emission over the range 300 to 600 nm, while the excitation wavelength was increased sequentially by 5-nm steps from 250 to 500 nm. Humification indices, according to both Ohno (2002) and Zsolnay (1999), were calculated allowing the comparison of the samples according to the degree of humification and the C/H ratio.

The results showed that single-scan fluorescence spectra are characterized by the presence of various main peaks. They show the presence of fulvic acids, aquatic humic acids, and natural organic matter (Cobble, 1996). Fluorescence excitation-emission matrices suggest the presence of protein-like substances in the sediment samples 3 and 4 while the presence of mainly fulvic-like substances in the samples 1 and 2.

Particulate organic carbon export on the east coast of the U.S.

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Organic matter production and export in the coastal ocean contributes significant fluxes of carbon to the biologic pump. On western boundaries where shelf break fronts are common, the mechanism for export of organic carbon is not well characterized. One such boundary, the Mid-Atlantic Bight, has been well studied and estimates exist for the export of organic carbon from the shelf to the open ocean. In addition, surface pCO_2 measurements have been used to determine that the region is a net sink for CO_2 (DeGrandpre et al, 2002).

A three-dimensional, nonhydrostatic, high-resolution model (Siedlecki et al, submitted) with idealized bathymetry is used to simulate the shelf and frontal circulations of an archetypical western ocean boundary off the east coast of the United States. A biogeochemical model is designed that predicts the biological production, f ratio, and

organic carbon flux to depth consistent with deep ocean observations. The addition of a second particle size to the model was critical in predicting all three variables.

Consistent with observations from the Mid-Atlantic Bight, the model predicts about 2-3% of the biological production is exported to the slope as large particles. The export occurs in the Ekman layers during both downwelling and upwelling events. The export of large particles contributes a significant flux of carbon to the biologic pump.

Distributions of the CO_2 system along the U.S. Atlantic and Gulf of Mexico Coasts

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Coastal oceans are a critical component of the global carbon cycle, and their capacity to absorb atmospheric CO_2 plays an important role in the global CO_2 budget. Coastal oceans are highly dynamic and heterogeneous due to complex physical, chemical, and biological forcings. The estimate of CO_2 flux from coastal oceans still bears large uncertainty due to limited data coverage around the globe. The greatest uncertainty in our understanding of the coastal carbon cycle surrounds biogeochemical mechanisms that control the coastal CO_2 source/sink.

As an NACP effort to improve our understanding of the coastal carbon cycle, NOAA conducted the Gulf of Mexico and East Coast Carbon (GOMECC) Cruise along the U.S. Atlantic and Gulf of Mexico coasts in July–August, 2007. This expedition was a systematic coastal carbon study with a focus on carbonate chemistry and carbon cycle processes over a wide range of oceanographic, atmospheric, and biogeochemical conditions. The cruise included a series of 9 transects approximately orthogonal to the Gulf of Mexico and Atlantic coasts and a comprehensive set of underway measurements along the entire transect. Full water column CTD/rosette stations were occupied at 90 specified locations. Herein, we will report the data of the CO_2 system parameters (pH, CO_2, total dissolved inorganic carbon or DIC, total alkalinity or TAlk) measured during the cruise.

There seem to be two general mixing regimes that exert significant controls on the distributions of the CO_2 system along the Gulf of Mexico and U.S. Atlantic coasts. One is dominated by the mixing between the Mississippi River and open ocean water, and the other is influenced strongly by combined effects of small-intermediate rivers, coastal marshes, and along-shore currents. Along with physical processes, biological processes also play an important role in controlling the spatial distributions of the CO_2 system. A significant CO_2 sink occurs in the northern Gulf of Mexico inside the plume of the

Mississippi River, where net biological uptake rate is the highest within the surveyed area. The CO_2 sink in other coastal areas is much smaller and less significant. The air-sea CO_2 flux will be estimated and integrated to assess its direction and magnitude for the entire eastern U.S. coastal area. The dominant biogeochemical processes that exert controls on the CO_2 flux will be discussed in detail by region and mixing regime. This study also aims to estimate dissolved inorganic carbon (DIC) export from the U.S. Gulf of Mexico and Atlantic coasts to the open ocean using different methods. To evaluate potential impact of ocean acidification on this coastal region, distributions of pH and $CaCO_3$ saturation state and their controlling mechanisms will also be examined. The GOMECC cruise provides a snapshot and baseline condition of the CO_2 system along the U.S. Gulf of Mexico and Atlantic coasts.