Ocean Carbon Biogeochemistry Workshop
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Poster Abstracts

Posters July 10, 2005:

Marine Ecosystem/Biogeochemical Dynamics:

Export of Particulate Organic Carbon Using ^{210}Po as a Metric – A Case Study from Bermuda Atlantic Time Series (BATS)

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Differences in the relative affinities of ^{210}Po and ^{210}Pb for biogenic particulate matter in the marine environment provides the basis in using ^{210}Po as a tracer for particulate carbon export from surface waters. Extensive work has been conducted using ^{234}Th as a POC export tracer, but the utility of ^{234}Th as a faithful POC export tracer has been frequently questioned. The ^{234}Th measured in particulate matter is mostly adsorbed Th, while organic carbon is primarily the major composition of the particulate matter. It has been shown that the global distribution of ^{234}Th-derived POC export fluxes can alone vary by 2-10 times or more solely due to the variability in the POC/$^{234}Th_p$ ratios. It would be ideal to have a tracer that tracks organic carbon for quantifying the export and regeneration of POC, and ^{210}Po is one such potential tracer.

We have collected a time series of water samples in vertical profiles of the upper ocean for the concentrations of dissolved and total ^{210}Po and ^{210}Pb and POC at or near the Bermuda Atlantic Time Series in the Sargasso Sea. The purpose is to determine the POC export using ^{210}Po/POC ratios as well as understand the geochemical cycling of ^{210}Po. In particular, we investigated the longer term, seasonal variations in the first-order scavenging residence times of surface biogenic particles. The concentrations of particulate and dissolved ^{210}Po, as well as the activity ratios of $^{210}Po/^{210}Pb$ were analyzed in the dissolved and particulate phases. We also evaluated the temporal variations of the inventories of particulate and dissolved ^{210}Po and ^{210}Pb, as well as the deficiencies of ^{210}Po with respect to ^{210}Pb. We have also collected time-series sediment trap samples to compare ^{210}Pb inventories with respect to inputs from atmospheric deposition and production from ^{226}Ra.

The percentage of particulate ^{210}Po was significantly higher than that for ^{210}Pb. The inventories of ^{210}Po in the upper 400 m varied almost by factor of 2, documenting seasonal variations of either atmospheric ^{210}Pb input or productivity removal of ^{210}Po. The $^{210}Po/^{210}Pb$ activity ratio in the filtered water samples was generally <1.0 in the upper 400 m. Consequently, the activity ratio in the unfiltered water samples often exceeded the equilibrium value of 1.0 at various depths, indicating biogenic particulate matter played a dominant role in the removal of ^{210}Po relative to ^{210}Pb. The first-order scavenging residence times of dissolved ^{210}Po and ^{210}Pb in the upper 400 m of the water column varied between 0.5 and 5.6 yrs, and 3.0 and 5.0 yrs, respectively. The seasonal variations of the residence times and export fluxes of ^{210}Po and ^{210}Pb will be discussed.

Climate-Related Interannual Variability of Potential New Production in the Western North Atlantic Ocean

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The North Atlantic Oscillation (NAO) is the largest single factor affecting climate variability over the western North Atlantic (WNA). Thus, it is reasonable to examine the effects of the NAO on carbon cycling in the region. However, an impediment to such work has been a lack of biogeochemical data that matches those available for the atmosphere and ocean, making assessment of the biogeochemical consequences of NAO-related climate variability difficult. Satellite-derived data, when used with our newly merged World Ocean Data (WOD) and Bedford Institute of Oceanography BIOCHEM data, along with diagnostic basin scale numerical modeling over the WNA is providing an opportunity to study the effects of the NAO on new primary production (NPP) over the relevant time and space scales. Our project is a three-year, data analysis and modeling effort aimed at understanding NAO-related interannual and decadal shifts of ocean circulation and availability of macro-nutrients (NO_3, PO_3, and ($Si(OH)_4$) and NPP for our WNA focus region. Our study is examining interannual and decadal variability of nutrients and NPP using potential new production (PNP) as proxy for NPP in WNA slope and shelf waters. Our study approach is to: (1) simulate the WNA physical circulation using a 1/6°, eddy-resolving, Regional Ocean Model System (ROMS) forced by characteristic low- and high-NAO heat fluxes and winds, (2) estimate macro-nutrient fluxes across the Gulf Stream (GS) and shelf-slope front (SSF) into slope and shelf waters using ROMS diagnostic velocity fields and objectively-analyzed (OA) biogeochemical fields from our combined WOD/BIOCHEM datasets; (3) compare our simulations with in-situ and satellite-derived data, including SeaWiFS and MODIS data; and (4) synthesize and develop our understanding of the NAOs impact on the underlying dynamic and biogeochemical processes. Herein, we report on our OA of the biogeochemical datasets and preliminary satellite data analysis and modeling results, including initial heat flux and winds used to force the model.

The Oceanic Flux Program (OFP) time-series: Seasonal and interannual variability of particle flux in the deep Sargasso Sea

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Since 1978, the Oceanic Flux Program (OFP) has continuously measured particle flux in the deep Sargasso Sea off Bermuda. The length of the current time-series (28 yrs) has allowed us to determine how temporal patterns of flux and its composition vary with depth and temporally over scales of weeks to decades, to capture rare, episodic extreme fluxes (e.g. large zooplankton blooms, hurricane-induced sediment advection off the Bermuda platform) that contribute to regional sedimentation, and to link flux patterns with changes in overlying physical and biological properties.

A prominent feature of the biweekly-resolved OFP record (since 1989) is the tight temporal and vertical coupling of the major flux constituents (carbonate, organic carbon, nitrogen, opal, and lithogenics) and the lack of any temporal phase lag in flux magnitude given the sampling resolution. Like precipitation, the frequency distribution of the deep ocean "rain" of particles is strongly skewed towards low fluxes and closely follows a theoretical gamma probability distribution. Strong seasonality is observed in flux variability as well as magnitude. During the low flux summer-fall season, flux frequency distributions are less strongly skewed and variable than during the high flux winter-spring season, where extreme flux variability (coherent with depth) is indicative of event-scale forcing of particle "rainstorms".

To assess interannual differences and long-term trends, we fitted monthly gamma probability distributions to the biweekly resolved flux data and recast the flux data as cumulative gamma probabilities. This approach implicitly incorporates the seasonal differences in flux frequency distributions thus enabling us to estimate the statistical probability of occurrence a particular flux magnitude with respect to the overall record. The analysis demonstrates (1) a high coherence in flux probabilities among depths (indicating strong vertical coupling) (2) low autocorrelation of flux on <monthly time scales (consistent with independent, event driven forcing), (3) periods of several months are often characterized by more frequent high or low flux extremes (suggestive of interannual differences in climatic forcing), and (4) minimal evidence for multi-year or decadal trends. Although evidence for long-term trends is weak, there is a small but statistically significant inverse relationship between the magnitude of annually-integrated (July-July) fluxes of carbon and nitrogen (but not carbonate) and the winter-time North Atlantic Oscillation (NAO) index. This inverse relationship, which is primarily driven by the magnitude of the winter-spring fluxes, correlates with higher variability in upper ocean mixing- both nutrient upwelling and downwelling- that is driven by an increased frequency of synoptic-scale storm passage at this latitude during the NAO low phase. We hypothesize that greater variability in upper ocean physical forcing decreases the overall coupling between organic matter generation and consumption, resulting in higher surface export fluxes and flux penetration with depth.

Sinking Particle Properties Determined From Image Analysis of Polyacrylamide Gels Deployed in Drifting Sediment Traps During KEOPS: Implications for Ecosystem Controls on Carbon Export in the Presence of Persistent Natural Iron Inputs

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The Kerguelen: Ocean and Plateau compared Study (KEOPS) examined the origin of elevated phytoplankton biomass over the Kerguelen plateau in the Southern Ocean in mid-summer (Jan. - Feb. 2005). Here we report sinking particle characteristics determined from image analysis of thousands of individual particles caught in viscous polyacrylamide gels placed in free-drifting sediment traps (at depths of 100, 200, 330, 430m) at two sites during KEOPS - the highest biomass site over the central plateau (A3), and a moderate biomass site at its periphery (C5). Based on morphology using low-power stereo-microscopy and image analysis, the particles were divided into three types i) marine 'snow' aggregates, ii) cylindrical faecal pellets , and iii) oval faecal pellets. We estimate that 2 to 11\% the sinking flux occurs in the form of discrete faecal pellets (median imaged areas ranging from .01 to .05 mm2 across all depths) at C5, and 21 to 34\% at A3, with the remainder in the form of large (.04 to .09 mm2) 'marine snow' aggregates. Because these aggregates are themselves predominantly formed from faecal pellets, the overall flux is controlled by grazing, rather than by phyto-detrital aggregation. This observation that the vast majority of the particle flux is processed through the heterotrophic foodweb, in this region of persistent iron inputs, contrasts with relatively small contributions from zooplankton to the control of carbon export as observed in short-term artificial iron fertilization experiments. The KEOPS results offer more appropriate scaling of the response of production and export to persistent iron fertilization than do short-term experiments.

Autonomous Near Real Time pCO_2/O_2 for UK Research Vessels

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Carbon dioxide (CO_2) is one of the major greenhouse gases in the atmosphere today and understanding its variability is critical to understanding both climate change and ocean acidification. Present atmospheric concentrations have reached their highest level in over 650,000 (or possibly 15 million) years. The ocean is one of the largest natural reservoirs of carbon and has buffered changes in atmospheric CO_2 by absorbing about half the CO_2 released by human activities since 1800. Therefore, understanding variability in air-sea flux of CO_2 is fundamental to predicting rates of climate change and ocean acidification. Partial pressure of CO_2 (pCO_2) in air and in the ocean are essential variables for calculating this flux. Globally there is a paucity of data in most ocean basins (especially the South Atlantic, Indian Ocean, South Pacific and Southern Ocean), as well as the shelf seas where knowledge of CO_2 fluxes is almost totally unknown.

Five autonomous pCO_2/O_2 instruments have been designed and built by the Plymouth Marine Laboratory and their commercial partners Dartcom. These machines will be installed on five UK research vessels (RRS James Cook, RRS Discovery, RRS James Clark Ross, RV Prince Madog and RV Plymouth Quest) and will send data in near real time via iridium. The data obtained by these underway systems, in both the global ocean and the shelf seas, will greatly help reduce the uncertainties in assessments of climate variability and impacts.

The Dissipation of a Deep, Poorly-Ventilated North Pacific Water Mass during the Last Deglaciation

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Theories to explain the drawdown of atmospheric carbon dioxide during the last ice age typically call on increased storage of carbon dioxide in the deep sea. However, evidence for this from the deep Pacific ocean, where the largest volume of deep water resides, has been lacking due to the paucity of suitable sediment records. We present new, multi-proxy evidence from sediment records in the deep subarctic Pacific (3 - 3.6 km), including benthic and planktonic foraminiferal ^{14}C and ^{13}C measurements, sedimentary U and Ba contents, calcium carbonate and opal abundance, and bulk sedimentary ^{15}N measurements. When taken together with previously published data, our results show the presence of a poorly-ventilated water mass during the glacial maximum, as long suspected but never proven. This water mass was strongly depleted in ^{14}C relative to the glacial atmosphere, was low in oxygen, had low $CO_3^{=}$ concentration and low ^{13}C, all consistent with high DIC concentrations. Meanwhile, above a deep chemical divide, the overlying waters were relatively oxygenated and nutrient-poor. At the midpoint of the deglaciation, the glacial deep water mass dissipated upwards in the water column, releasing CO_2 from storage, enhancing the preservation of deep carbonate and shifting nutrients into the thermocline. The flux of nutrients into the upper ocean associated with this breakdown of the deep water mass enhanced biological activity throughout the North Pacific. The resulting boom in export production intensified the thermocline oxygen minimum zone, accelerating denitrification and the production of nitrous oxide. This led to the modern configuration of a relatively well-ventilated deep sea, overlain by an oxygen minimum.

Satellite Derived Weekly 0.25 x 0.25 Degree Caribbean Region Sea Surface $fCO_{2,sw}$ Fields

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Weekly fields of sea surface carbon dioxide fugacity (fCO_{2sw}) have been modeled for the Greater Caribbean Region starting from 01 June 2002. The model is based on empirical relationships derived using shipboard $fCO_{2,sw}$ and sea surface temperature (SST) measurements taken aboard the *Explorer of the Seas* operated by the Royal Caribbean International. The *Explorer of the Seas* has been equipped with meteorological and oceanographic instruments maintained by the University of Miami's Rosenstiel School of Marine and Atmospheric Science and Atlantic Oceanographic and Meteorological Laboratory (AOML) of the National Oceanic and Atmospheric Administration (NOAA) and has been making alternating western and eastern cruise tracks throughout the greater Caribbean Sea with an underway fCO_2 analyzer since February 2002. The model is constrained using remotely sensed SST, wind speed, estimates of atmospheric CO_2 partial pressure ($pCO_{2,air}$), and sea surface salinity. The resulting model is given by,

$$fCO_{2,sw} = \left(\frac{1}{e^{\beta_1 W_s}}\right)\left(e^{\beta_2 SST} + \beta_3 k_o\right) + pCO_{2,air}$$

The temperature and salinity dependent gas solubility (k_o) is estimated using NODC monthly climatology's of sea surface salinity. The weekly mean wind speed normalized to 10 m height (W_s) is obtained from 25-km resolution QuickSCAT science level L3 wind vector data from the Physical Oceanography Distributed Active Archive Center (PO.DACC) of NASA/JPL. Atmospheric CO_2 partial pressure ($pCO_{2,air}$) was computed from dry atmospheric CO_2 mole fraction data (XCO_2) obtained from the NOAA/CMDL carbon Cycle Greenhouse Gases Group flask sampling program and gridded fields of daily mean seal level pressure (SLP) obtained from the NOAA-CIRES Climate Diagnostics Center. Spatial $fCO_{2,sw}$ fields have been generated using the Remote Sensing Systems microwave optimally interpolated blended SST product. Comparisons between shipboard measurements and co-located model estimates indicate that the present model accounts for ~75% of the variability and exhibits an RMS of ±10 µatm. NOAA Coral Reef Watch is working to couple the offshore modeled fields of $fCO_{2,sw}$ to *in situ* observations of fCO_{2sw} overlaying coral reef ecosystems. The modification of the overlying CO_2

system relative to the source waters offshore can be used as a proxy of the integrated metabolic processes occurring at the reef. Extended monitoring of this parameter at select US coral reef sites will permit NOAA to track changes in the metabolic performance of these ecosystems as they respond to various climate related stresses such as increased incidence of coral bleaching due to rising thermal stress and reduced calcification rates in response to ocean acidification.

Climate Controls on Carbon Export in Ocean Basins of the Northern Hemisphere as Viewed from Space

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We have developed a method that makes it possible to map nitrate-based new production at local, regional and basin scales using remote sensing data. These maps have been utilized extensively in the North Pacific Ocean, where they have helped understand how changes in the strength of the Aleutian Low following the onset of El-Niño conditions in the tropics and disturbances in the overlying atmosphere impact new production in the subarctic Pacific. In more recent studies, we have used these maps to detect climate-mediated changes in carbon export in the North Atlantic Ocean and in the Arabian Sea. In the North Atlantic Ocean basin, where ocean circulation during winter is largely governed by the strength of the North Atlantic Oscillation (NAO), and nitrate inputs are primarily from winter convective mixing, our maps show enhanced (reduced) carbon export during strong negative (positive) phases of the NAO. In the Arabian Sea, these maps provide the first indications that anomalies in the strength of the monsoon winds associated with the warming trend over Eurasia, are likely to increase biological productivity and carbon export in the northern Arabian Sea.

Timing of Nutrient Depletion, Diatom Dominance and A Lower-Boundary Estimate of Export Production for The Irminger Basin, North Atlantic

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During the North Atlantic spring bloom, a seasonal phytoplankton community succession takes place from diatoms to non-siliceous phytoplankton. Diatoms rely on silica to form their frustules and are out-competed by other species when silica becomes depleted. Diatoms are also expected to contribute significantly to export production in the North Atlantic. We suggest that a lower boundary to export production can be estimated as the component of total production that occurs between the start of the spring bloom and the time when silica becomes depleted. This method has been tested in the Irminger Basin, located between Greenland and Iceland, in the North Atlantic. A technique to estimate silica concentration from satellite-derived sea surface temperature and chlorophyll *a* concentration has been developed and used to determine silica concentration at high spatial and temporal resolution. This facilitates an estimation of the timing of silica depletion and thus the timing of the transition from a phytoplankton community dominated by diatoms to dominance by non-siliceous species. The timing of the initiation of the bloom, defined as a pronounced and sustained increase in biomass, is estimated from a Sea-viewing Wide Field-of-View Sensor (SeaWiFS)-derived chlorophyll *a* concentration. A lower-boundary estimate of export production is made and, additionally, estimates of the contribution to export production by diatoms and non-diatoms are made by considering silica-to-nitrate drawdown ratios. We estimate export production in this region to be ~60 gC m^{-2} yr^{-1}, of which diatoms account for ~65%.

SIBER: Sustained Indian Ocean Biogeochemical and Ecological Research

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The Indian Ocean (IO) has two unique characteristics that profoundly impact its biogeochemical cycles. The first is the northern land boundary, which precludes significant thermocline ventilation in the north. The second unique feature is the annual monsoon cycle and the seasonal evolution of oceanic current patterns and upwelling. Combined, these two features give rise to seasonal biogeochemical cycles that are driven primarily by the monsoon cycle, and that are highly asymmetric across the equator. There are also very significant biogeochemical differences between the two northern sub-basins, the Arabian Sea and the Bay of Bengal. For example, the Arabian Sea includes an extensive mid-depth oxygen minimum zone (OMZ) that is one of three prominent open ocean suboxic regions where globally significant denitrification occurs. In contrast, the Bay of Bengal is subject to large seasonal freshwater inputs with attendant anthropogenic nutrient loading. In recent years there has been growing interest in the climate of the IO basin as a whole, following the identification of the IO Dipole/Zonal Mode (IODZM). In addition, over the last few decades the IO has warmed systematically by over 1º C, one of the most significant regional trends and hence a potential indicator of global warming. Yet compared to the Atlantic and the Pacific, our knowledge of the biogeochemical dynamics of the IO is rudimentary, at best. Major gaps in our understanding include insufficient characterization of CO_2 exchange between the atmosphere and the ocean, unknown biogeochemical response to systematic warming, large uncertainties about the role of Fe limitation and its impact on carbon drawdown, and a rudimentary understanding of the biogeochemical response to the IODZM.

The overarching goal of the SIBER (Sustained Indian Ocean Biogeochemical and Ecological Research) initiative is to promote and plan future biogeochemical and ecological research in the IO. The SIBER workshop will convene an international, interdisciplinary group of scientists at the National Institute of Oceanography in Goa, India (October 3-6, 2006) to: 1) review the state of our scientific understanding of the biogeochemical and ecological dynamics of the Indian Ocean in relation to geography and physical forcing; 2) identify prominent gaps in our knowledge; and 3) formulate a plan for future biogeochemical and ecological research that substantially leverages the planned CLIVAR/GOOS Indian Ocean observing system.

Posters July 11, 2005:

Ocean Carbon Sequestration Concept Using Wave-Driven Deep Ocean Pump System

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Anthropogenic CO2 buildup is indisputable and is the leading cause of global warming as evidenced by melting glaciers and arctic ice, and warming of the oceans. The increase in CO2 comes from consumption of fossil-fuels - likely to continue for centuries from increased energy demand by our growing population and rapidly expanding third world economies.

Current research is focused on geologic sequestration of CO2 - putting the "carbon back in the ground from whence it came." But the potential for oceanic uptake of CO2 is magnitudes greater than geologic sequestration, if methods can be developed, and if the environmental consequences of oceanic sequestration are neutral. Two ideas have been proposed for oceanic sequestration: 1) Widespread iron fertilization of the ocean to increase primary production which absorbs CO2; and 2) Capture CO2 from fossil-fired electrical generators and pipe it to the ocean depths where it liquifies and sinks, forming lakes of liquid CO2 on the ocean floor.

We are developing a different approach conceptually similar to iron fertilization, but more beneficial. Our device is a wave-driven deep ocean pumping system to bring up higher-nutrient deep ocean water to increase primary production and thus CO2 absorption. The pump consists of a buoy connected to a base with valve, and a flexible tube which conveys deep, cold and nutrient-rich water to just below the surface. On wave upslopes the valve closes and the entire column of water is elevated; on wave downslopes the valve opens, replenishing the cold, nutrient-rich water inside the base. Pumps are deployed in arrays, tethered at the base to maintain relative position, and periodically seafloor-anchored to maintain position of the array. Thousands of pumps can be deployed efficiently using barges. Pumping rate is a function of tube size, wave height and period. Depth can be modified according to the local ocean biochemical profile. The buoys have solar-powered communications/control, allowing them to be activated by remote control using a satellite uplink. Pumps would not be deployed in shipping lanes or near shore.

In a global system with 200 arrays of pumps of 100km by 100km and pump spacing of 200m, the total number of pumps is 5 million. The 200 arrays would cover two million km^2, or 0.55% of the 362 million km^2 ocean surface. With estimated deployed pump cost of $2,000, the total investment is $10 billion, plus annual maintenance costs estimated at 33% or $3.3 billion. To achieve desired CO2 absorption, this conceptual system can be scaled up or down.

While the upfront cost is substantial, we believe the benefits are much greater given the enormous potential damages of global warming from melting icecaps, weather changes, environmental destruction, etc. As cost-offsets, we would expect improved ocean fisheries as the enhanced growth of phytoplankton propagates up the food chain; and, if strategically positioned in hurricane-prone regions, the cooling of the upper ocean mixed layer in the path of a hurricane could reduce intensity with less damage from high winds, heavy rain, and storm surges.

Web-Accessible Visualization and Extraction System (WAVES) for Oceanographic Data
Alex Kozyr

WAVES V1.0 is a web-based, database driven tool for oceanographic data (discrete measurements only at this time) extraction lets users to choose what kind of data they want to get and in which format. The interface has only one front page and all on-screen results are shown in a new window. Main page is divided in sections that help to navigate and keep different types of parameters grouped. In Query Parameters section users can set up search criteria's and limitations. Single parameters, for example temperature from/to: 25ºC, can be used as well as a range of parameters, e.g. temperature from: 20ºC to: 25ºC. The data location coordinates can be entered manually or dragging a box on the map (icon with "i"). Map is tightened to Geographical Region, Section, and Cruise ID drop-down-menus and all changes are reflected on the map.

Output parameters section has list of all variables that can be extracted from the database. Clicking a checkbox next to the variable name users may choose parameters that they need or chose all parameters clicking on "Check All" box.

Format in which requested information will be presented is set up in the Output Form section. Users have options to get it as an on-screen table, as a downloadable file (CSV, TSV, NetCDF formats) or as an on-screen property-property plots.

Interactive map is designed to provide the metadata information which displayed in the clickable Metadata section by using an Information mode (icon with "i") Users can receive metadata information by clicking on a cruise line, or dragging a box in the research area of the map. The access to metadata provided through the same interface using the background connection to metadata search engine *Mercury*. Map has also a Navigation mode (icon with palm). In Navigation mode users can move map around (by dragging) Also users could zoom it in (icon with +), zoom it out (icon with -) the map, and see the whole extend (icon with an arrow).

Architecture of WAVES is based on the following components: php engine, MySQL database, Subsys_JsHttpRequest library, Minnesota Map server, and ka-Map server.
Php engine with DHTML and JavaScript is used as the main tool for interface creation, data extraction and forming results pages.

The WAVES is now available for use through CDIAC web page at:
http://cdiac.ornl.gov/oceans/search.html

Satellite Assessments of Air-Sea Fluxes of CO_2 in a River-Dominated Coastal Margin
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A major objective of the U.S. Global Change Research Program Climate Change Science Program Strategic Plan and the North American Carbon Program is the application of satellite ocean color to characterize the spatial variability of air-sea CO_2 flux in the oceans adjacent to the North American continent. Recent studies in the northern Gulf of Mexico and elsewhere demonstrate that enhanced biological production in large river plumes may lower surface pCO_2 levels such that these regions may exhibit a net surface influx of atmospheric CO_2. Systems are likely to differ depending on the both biological and chemical properties and quantification of the contributions of river-influenced margins to regional CO2 fluxes is difficult due to the high degree of spatial and temporal variability in these regions. Satellite-based regional approaches can be used to extend the spatial and temporal coverage for broad scale assessments of pCO_2 distributions and air-sea fluxes of CO_2. The primary objective of our research is to apply these approaches to the characterization of pCO_2 and air-sea fluxes of CO_2 in the river influenced margin of the northern Gulf of Mexico.

We have successfully developed and applied an algorithm for assessment of areal distributions of pCO_2 from MODIS imagery in the northern Gulf of Mexico based on empirical relationships of in situ measurements of surface pCO_2 to environmental variables (T, S, chlorophyll). We applied principal component analysis to the T, S and chlorophyll data and regressed the derived orthogonal components against pCO_2 to produce an empirical algorithm for the estimation of pCO_2. Initial results from June 2003 revealed regions of low pCO_2 near the river plume, which would indicate net uptake in those regions. Physical mixing of river and ocean waters alone cannot account for observations of pCO_2 below atmospheric levels, evidence for a strong river biological pump. Subsequent cruises in August 2004 and October 2005 revealed a different pattern with generally higher levels of surface pCO_2. Satellite-derived regional assessments of pCO_2 were used in conjunction with estimates of wind fields to produce regional-scale estimates of air-sea fluxes. There was net uptake of CO_2 in June, but a net release in August and October.

Overall, our results were encouraging for the use of satellite approaches to improve regional assessments of coastal carbon budgets. Variability in conditions in coastal waters poses a challenge in that it limits the generality of algorithms across temporal and spatial ranges. This may be addressed by providing more in situ data, including ship-based surveys and moored time-series.

Net Community Production in the Ross Sea Polynya

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The Southern Ocean is generally regarded as a net sink for atmospheric CO_2; however, the magnitude and variability of this sink are not well known. Southern Ocean C transfer hotspots include large continental shelf polynyas and the Antarctic Polar Frontal Zone. Situated over a broad continental shelf, the Ross Sea includes the most productive areas in the Southern Ocean, supporting large blooms of both diatoms and the prymnesiophyte *Phaeocystis antarctica*. These two algal groups play intriguing and different roles in the biogeochemical cycles of nutrients and carbon in the Ross Sea, and by extension, other polynyas and ice marginal environments in the Southern Ocean; these may exert an important influence on climatic variability in the past and future. Here we present recent measurements of *p*CO2, total dissolved inorganic carbon (DIC), and nutrient concentrations from the Ross Sea polynya. Integrated seasonal DIC drawdown in the upper 150 m of the water column, corrected for air-sea gas exchange, is used to estimate net community production (NCP). Variability in NCP is related to changes in phytoplankton community composition as well as mixed layer dynamics. NCP is compared to the standing stock of particulate C to calculate export into high salinity shelf waters. Previous work and our own calculations suggest that much of the seasonal C export is remineralized and mixed throughout the Ross Sea water column during the austral autumn and winter. However, we explore scenarios wherein the retention and subsequent export of biologically fixed CO_2 is enhanced.

A Flexible C:N:P Ratio Model of the Microbial Loop in the Open Sea

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The microbial loop schemes in most marine biogeochemical models are relatively simple and do not represent current understanding of the microbial loop. We constructed a new microbial loop model to include these features. The model simulates the carbon (C), nitrogen (N) and phosphorous (P) components in picophytoplankton, bacteria, protozoa, metazoa and labile and semi-labile dissolved organic matter (DOM), and inorganic nutrients including ammonium, nitrate and phosphate. The C, N and P are tracked independently so that the C:N:P ratios in the compartments are flexible. The model represents bacterial processes differently from previous models mainly in four ways including: 1) continuous lability of semi-labile DOM determined by nutrient contents, 2) selective semi-labile DOM uptake by bacteria, 3) continuous inorganic nutrient limitation on bacterial growth even if DOM is enriched in nutrients, and 4) variable bacterial growth efficiency depending on bacterial production. We tested the performances of the model by applying it to the Hawaii Ocean Time-series (HOT) site. It runs in the surface 100 m as a box model until achieving steady state, which is used to compare to the average HOT observations. Some of the initial N and P contents are based on the average HOT observations, and the total N and P are conservative in the model by compensating N and P export with nitrate and phosphate inputs, while C content is open through primary production and export. The model was tuned to approach observed semi-labile DOC standing stock by adjusting lability parameters for DOM. In the steady-state results, the standing stocks and stoichiometry of biological compartments and inorganic nutrient concentrations are comparable to the HOT observations, supporting our new schemes. The experiments indicated that semi-labile DOM and inorganic nutrients are most sensitive to the model parameters, and the parameters related to DOM lability and bacterial selection on DOM uptake are most important. In an initial result, semi-labile DOM supported >75% of bacterial production. A revised model, with nearly 50% of BP supported by semi-labile DOM was closer to observations. These results point up the importance of semi-labile DOM in ocean nutrient cycling. Our results suggest the system at the HOT site is still N-limited.

Phytoplankton-Light Feedback and Climate Change : Polar Surprises?

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The photosynthetic activity of oceanic phytoplankton implies light absorption and thus its control on light and heat penetration with potential impact on upper ocean physical properties. Consequently, a feedback between ocean biology and physics is thought to establish because ocean physics controls phytoplankton dynamics through light and nutrient availability.

Our previous modeling results (Manizza *et al.*, 2005) show that this feedback amplifies the seasonal cycle of sea surface temperature and consequently that of sea-ice cover (SIC) in an ocean model for present climate conditions.

Climate models (Sarmiento *et al.*, 2004) predict a change in the geographical distribution of phytoplankton biomass at global scale due to climate change. This change might alter the functioning of phytoplankton-light feedback compared to present-day conditions.

We explore this potential change using a global Ocean Biogeochemical General Circulation Model(OBGCM) that prognostically computes both physical and biological variables to represent this biogeophysical feedback. We force our OBGCM with an atmospheric forcing accounting for climate change following the A2 IPCC Scenario of CO2 emissions for the period 2005-2061.

We focus on the polar oceans only. The oceanic heat uptake, greater in the Arctic than in the Antarctic Ocean, determines a faster SIC melting in summer while climate change progresses. In the Arctic Ocean, consequently this faster SIC melting weakens the melting effect due to the biogeophysical feedback that still remains unchanged in the Antarctic Ocean.

This effect creates a clear imbalance in the amplification of seasonal cycle of the Arctic SIC with a clear dominance of the forming winter effect (up to 4 %) on the melting summer effect (up to 0.5 %).

These results show a clear interaction between this feedback and climate change in the polar oceans and its asymmetrical behavior between the two poles. The present results encourage for further numerical experiments with an interactive atmospheric component given that SIC controls albedo and this effect might also influence the radiative budget of the earth's atmosphere.

Satellite-derived Distributions of DOC and CDOM in the U.S. Mid-Atlantic Bight

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Dissolved organic carbon (DOC) in the ocean constitutes a major global carbon reservoir. In coastal ocean waters, distributions of DOC vary seasonally and inter-annually due to multiple source inputs including *in situ* primary production, contributions from adjacent ocean waters, and terrigenous, anthropogenic and estuarine-derived organic matter entering the coastal ocean from rivers and bays, and removal processes such as advection, microbial remineralization and photo-oxidation. Chesapeake Bay, as one of the largest and most productive estuaries in the world, can influence the carbon cycle of the adjacent continental margin through contributions of carbon and nutrients. We conducted several cruises in 2005 between the mouth of Chesapeake Bay and continental slope waters within the U.S. Mid-Atlantic Bight (MAB) to examine the impact of Chesapeake Bay and adjoining watersheds on distributions of DOC, particulate organic carbon and chromophoric dissolved organic matter (CDOM) and the export of terrigenous carbon to the continental margin. One of our objectives is to apply our *in situ* data to develop algorithms to retrieve CDOM and DOC from MODIS and SeaWiFS satellite observations. In order to develop empirical algorithms for CDOM and DOC, we correlated the CDOM absorption coefficient (a_{CDOM}) with *in situ* radiometry (reflectance band ratios) and then correlated DOC to reflectance band ratios through the CDOM to DOC relationships. Preliminary results demonstrate that we can retrieve a_{CDOM} through empirical relationships similar to those described by D'Sa and Miller

(2003) and Johannessen et al. (2003). Because of seasonal differences between the DOC-a_{CDOM} relationship, at least 2 seasonal algorithms for DOC will be required (winter-spring and summer). Our analyses indicate that DOC and a_{CDOM} can be retrieved from coastal ocean waters with Aqua-MODIS to within 15% and ~25% uncertainties on average, respectively. With accurate satellite retrievals of CDOM and DOC, we will be able to apply satellite observations to investigate interannual and decadal-scale variability in surface CDOM and DOC concentrations within the MAB and quantify the DOC reservoir and seasonal net community production of DOC.

Modeling the Seasonal Cycle of pCO_2 in the North Atlantic

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Capturing the seasonal cycle of surface ocean pCO_2 is a challenge for ocean biogeochemical models in the high latitude North Pacific (McKinley et al. 2006). Models are particularly challenged to capture the full amplitude of wintertime DIC supply to the surface ocean and the seasonal drawdown of DIC associated with the spring bloom in regions where data suggest this cycle is particularly vigorous. This is a concern because the same mechanisms that determine the seasonal cycle also control interannual to decadal timescale variability, but data is scarce to act as a direct longer-term constraint. We have begun to investigate seasonal pCO_2 processes using a North Atlantic regional model at ½ degree resolution with an embedded 2 functional group ecosystem that includes explicit cycling of phosphorus, silicate, iron, oxygen, carbon and alkalinity. We report on initial model – data comparisons and efforts to improve the model's pCO_2 seasonal cycle.

Trace Metal Deficiency and Suboxia Limit Productivity of Upwelled Water in the Arabian Sea

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Summer-time upwelling of subsurface waters along both the eastern and western boundaries of the Arabian Sea has been known to cause large-scale fertilization of euphotic zone and widespread phytoplankton blooms, but a direct comparison of the intensity and biogeochemical impact of this process over the two margins has not been possible so far due to lack of data. We carried out the first-ever survey covering, with the same vessel and during the same season (late southwest monsoon of 2004), the Indian and Omani continental shelves as well as open Arabian Sea, and observed much lower rates of primary production (PP) than would be expected in macronutrient-replete upwelled waters. Contrary to the prevalent belief, over the well-ventilated Omani shelf PP appears to be at times limited by low levels of iron, the uptake of which by phytoplankton may be further inhibited by extremely low copper concentrations. By contrast, along the Indian coast, where the upwelled water loses all dissolved oxygen (O_2) due to a longer residence time, elevated PP occurs only within a thin oxygenated layer, implying that even though phytoplankton produce O_2, its unavailability for metabolic requirement may inhibit their growth. These measurements of PP, combined with more extensive chlorophyll and hydrographic data, when compared with the JGOFS observations, do not support the recently reported intensification of upwelling and large enhancement of phytoplankton biomass in the Arabian Sea linked to a decrease in the winter/spring Eurasian snow cover since 1997. Trace-metal limitation of PP in the western Arabian Sea has potentially important implications for regional biogeochemistry including the formation and future evolution of the globally-significant denitrification zone.

Increase of Anthropogenic CO2 in the Atlantic Ocean over Last Few Decades
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The carbon data collected during the GEOSECS program in early 1970s represent results of the first systematic survey of inorganic carbon parameters on a global scale. Based on this historic data set, the subsequent carbon data collected during TTO, SAVE, WOCE/JGOFS, and CLIVAR/CO2 Repeat Hydro programs in the Atlantic Ocean can be used to study the temporal variations of carbon and other geochemical properties. It is essential that the historic GEOSECS data set is consistent with recent high quality carbon data resulting from improvements in measuring techniques and the use of reference material. Results of re-evaluation of GEOSECS carbon data in the Atlantic Ocean by examining deep water properties at crossover stations between GEOSECS and WOCE cruises show that DIC measurements made in GEOSECS program are systematically higher than those made during recent WOCE/JGOFS global CO_2 survey. In the North Atlantic, the overall average offset is estimated to be 27 ± 9 µmol/kg for DIC north of 15°N. In the equatorial region between 15°N and 15°S, the mean DIC offset is 9 ± 11 µmol/kg, and in the South Atlantic is 5 ± 5 µmol/kg south of 15°S. Applying Multi-parameter Linear Regression method (MLR) to WOCE carbon data, DIC in the three latitudinal regions of both west and east basins in the Atlantic Ocean is derived as a function of potential temperature, salinity, AOU, and nutrients (Silica and PO_4). After correcting GEOSECS DIC data, a residual DIC is computed between adjusted DIC and predicted DIC using the DIC equations derived from WOCE carbon data. The preliminary results of estimating the increase in anthropogenic CO_2 based on these residual DIC indicates that the mean anthropogenic CO_2 uptake rate in the Western basin is 0.70 mol/m^2/yr for the region north of 15°N, 0.53 mol/m^2/yr for the equatorial region, and 0.83 mol/m^2/yr in the south Atlantic. In the Eastern basin, the mean CO_2 uptake rate is estimated to be 0.97 mol/m^2/yr for the north Atlantic north of 15°N, 0.57 mol/m^2/yr for the equatorial region, and 0.28 mol/m^2/yr for the south Atlantic south of 15°S. The uncertainty of these estimates is high due to un-sufficient GEOSECS data and the quality of these background data is not as good as recent WOCE data. We are in the process of analyzing the anthropogenic CO_2 increase using comparison of salinity normalized DIC after correction for AOU along the isopycnal surfaces representing the upper thermocline waters. Any preliminary results will be presented at this Ocean Carbon Biogeochemistry workshop.

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Measuring the Residence Time of Dissolved Organic Carbon through Compound Specific Radiocarbon Analyses of Dissolved Polysaccharides

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Numerous studies show that bacterial production is limited by the availability of labile dissolved organic carbon (DOC), even though the ocean stores a vast quantity of organic carbon in the dissolved phase (600-700 GT C), and DOC concentrations are high throughout the water column (40-80 μM C). The large reservoir of DOC that accumulates in seawater is believed to cycle on decadal to millennial time scales, and is therefore unimportant in supporting bacterial carbon demand. We measured the natural abundance radiocarbon values of pure sugars isolated from high molecular weight DOC to determine their residence time in seawater. In the upper mixed layer at two locations in the North Pacific Subtropical Gyre, we found that dissolved polysaccharides have radiocarbon values of 89 ± 13 per mil and 57 ± 6 per mil, equal to DIC at these sites. If dissolved polysaccharides were cycling on decadal timescales, we would expect them to be enriched in radiocarbon relative to DIC due to the large pulse of radiocarbon delivered to the upper ocean by atmospheric testing of nuclear weapons. A simple box model for radiocarbon in DOC was developed to show that dissolved polysaccharides cycle on annual time scales, and that they support a significant faction of annual bacterial carbon demand in the open ocean.

Small Phytoplankton and Carbon Export in the Open Ocean

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Autotrophic picoplankton are often the dominant primary producers in oceanic regions but are thought to contribute relatively little to the export of carbon from surface layers because of their small size, slow sinking rates, and active involvement in recycling through the microbial loop. Using inverse and network analyses of data from the equatorial Pacific and Arabian Sea, we show that the relative contributions of picoplankton to carbon export are not always low but are linearly related to their contributions to total primary production. Structures of modeled food webs historically preclude potentially important pathways for the export of picoplankton, including the direct sinking of aggregated ungrazed cells and the consumption and subsequent export of aggregated picoplankton via large grazers. Here, we propose a conceptual view wherein all primary producers contribute to one pool of carbon with the ultimate source of exported carbon being directly proportional to the size class of the primary producer.

An Ocean Colour Inherent Optical Property Model: Description, Validation and Application

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Over the past twenty years, ocean colour satellites have given insight into the biological activity within the global ocean at unprecedented spatial and temporal scales. Initially these data were applied to empirical derived relationships between the measured reflectance ratios and surface chlorophyll concentrations enabling a first guess at the biomass and hence primary productivity of the global ocean. Increasing algorithm complexity led to a plethora of new products, other than chlorophyll, such as Coloured Dissolved Organic Matter (CDOM) and Suspended Particulate Matter (SPM) to be derived. Recently the emphasis has been squarely on determining the Inherent Optical Properties (IOPs) of seawater, i.e. its absorption and scattering, from satellite data using analytical techniques with recourse only to empiricism where mechanisms or parameterisations are poorly understood.

This paper presents a new semi-analytical approach to the problem of determining IOPs from satellite using empirically derived spectral slopes between neighbouring wavebands in combination with radiative transfer modelling. This results in values of the total absorption and backscatter, together with the components of absorption due to phytoplankton and CDOM. Validation of this model against the NOMAD database of 400+ points shows the model to make excellent retrievals of total absorption and backscatter across the entire spectrum with slopes close to unity, little or no bias, high percentage of variance explained and low RMS errors.

Finally we present the application of this model to satellite data, showing its sheer power for determining primary productivity, underwater visibility, oceanic heat fluxes and phytoplankton functional types.

Elevated Atmospheric CO_2 Increases Growth Rates in the Diatom *Thalassiosira pseudonana* But Decreases Resistance to UVR Exposure

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Predicting the impact of increased atmospheric CO_2 concentrations on aquatic ecosystems requires an understanding of its effects on phytoplankton growth and photosynthesis. The response of primary productivity to increased CO_2 varies among species due to different affinities for CO_2. However, most studies have focused on few phytoplankton species and little is known about the effects of other environmental variables. We studied the effect of increased CO_2 on light absorption, cell permeability, growth and carbon fixation under PAR and UVR exposures in the diatom *Thalassiosira pseudonana*. Susceptibility of photosynthesis to UVR exposure was estimated from incubations in a UVR polychromatic incubator that uses a solar simulator lamp (Xe-lamp). These data allowed the estimation of P-I curves and Biological Weighting Functions (BWFs) for inhibition of photosynthesis, respectively. Nutrient replete cultures were acclimated to present CO_2 atmospheric levels (0.03% CO_2) and predicted future high CO_2 levels (0.1% CO_2) under PAR and UVR exposures. Changes in cell permeability were assessed by changes in fluorescence emission using the membrane potential dye $DiBAC_4(3)$. For the light intensities used, UVR exposure during growth did not affect rates of growth and photosynthesis, but decreased the sensitivity to UVR in both high and low CO_2 cultures. Cells showed decreased photosynthetic efficiency and increased cell permeability during the first 4 days after transfer to elevated CO_2. Subsequently, increased CO_2 enhanced growth and photosynthesis, but significantly decreased chlorophyll concentration. In addition, the BWFs showed that cells grown under high CO_2 were more sensitive to UVR. The results imply that high CO_2 conditions induced the downregulation of the photosynthetic machinery in *T. pseudonana* increasing the resource use efficiency. However, it is likely that the downregulation also affected the synthesis of repair enzymes therefore increasing the susceptibility of the cells to UVR damaging exposures.

Multispectral Remote Sensing Algorithms for Particulate Organic Carbon (POC)

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Hydrographic data, combined with continuous beam attenuation profiles and discrete measurements of particulate organic carbon (POC) from the Northeastern Gulf of Mexico (NEGOM) study, were used along with remotely sensed measurements from NASA's Sea-viewing Wide Field-of-view Sensor (SeaWiFS) to develop algorithms to estimate POC concentration. Algorithms have been developed successfully for Case I waters to estimate POC concentration using SeaWiFS ocean color products such as chlorophyll concentration, diffuse attenuation coefficient at 490 nm, and single-wavelength or ratios of multiple wavelengths of normalized water-leaving radiances *Lwn* (or remote-sensing reflectance *Rrs*). Using the ratio of multiple wavelengths (or reflectance) to estimate POC concentration yields smaller errors than estimates based on a single wavelength. While the single- or few-wavelength algorithms provide reasonable POC concentration estimates in Case I waters, they are less accurate in Case II waters due to non-linear responses of upwelling radiance from particulate and dissolved constituents. Therefore, in Case II waters, the maximized simple ratio (MSR) algorithm provides a more robust estimate of POC concentration. The algorithm derived estimates of POC concentrations matched well the spatial and seasonal distributions of POC measured *in situ* in the Gulf of Mexico.

CARBOOCEAN-the European Motor for Marine Carbon Cycle Research

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CARBOOCEAN is an Integrated Project (IP) funded by the European Commission (contract 511176-2) with 14.5 Million EUR over a 5 year period to assess the marine carbon sources and sinks with special focus on the Atlantic and Southern Oceans of -200 to +200 years

from now. It combines the key European experts in the field from 14 countries and cooperates with 7 research institutes from the US. Data is made available through the CARBOOCEAN data portal, a search engine which uses a distributed
network database that allows access to the data holdings from all partners involved (CDIAC, IFREMER, WDC-MARE).

CARBOOCEAN will investigate the following unresolved questions: How large are the Atlantic and Southern Ocean CO2 sinks precisely? What do European rivers and shelf seas contribute to the large scale CO2 sources and sinks pattern of the North Atlantic Ocean in relation to uptake within Western Europe? What are the key bio-geochemical feedbacks that can affect ocean carbon uptake? What is the quantitative global and regional impact of such feedbacks when forced by climatic change in the next 200 years? With respect to FP7, imperative attention will also be paid to pCO2 sink monitoring, ocean acidification assessment, and biogeochemical feedback quan-tification.

In cooperation with CarboEurope IP, CARBOOCEAN IP will generate the missing scientific knowledge that is essential to a global quantitative risk/uncertainty judgment on the expected consequences of rising atmospheric CO2 concentrations. In order to involve both policy and the general public both IPs created "CarboSchools".

Air-Sea CO_2 Fluxes in the Caribbean Sea

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A major goal of international ocean carbon research is to determine regional fluxes on seasonal timescales to assess the magnitude and changes in atmospheric CO_2 uptake by the ocean. This effort requires sustained observations of surface pCO_2 as well as a means to interpolate the observations in time and space. From a combination of weekly shipboard measurements of surface water pCO_2 and remotely sensed parameters, weekly flux maps have been created for the Caribbean Sea for the past three years. The pCO_2 measurements were performed on the cruise ship Explorer of the Seas operated by the Royal Caribbean Cruise lines who have installed an oceanographic laboratory on this ship.

For each year a correlation between pCO2 and SST is established using temperature data from the thermosalinograph located near the seawater intake on the ship. This relationship is then combined with the regional 1 by 1 ° weekly temperature data assimilated using *in situ* observations and AVHRR temperature data [*Reynolds, 2002*] to create weekly pCO_2 fields. These pCO_2 fields are combined with wind speeds from the SeaWinds sensor on QuikSCAT to estimate the weekly regional fluxes. The data from 2002 and procedures are detailed in Olsen et al. [2004]. Here we augment these results with observations from 2003, 2004, and 2005 *[Wanninkhof et al., 2006]*. The algorithms between pCO_2 and SST are very similar for the 4 years. However, annual changes in SST results in significant differences in annual fluxes. The annual fluxes for the Caribbean (15-30 ˚N, 60-90 ˚W) are estimated at:

2002 = -4.8×10^{11} mol
2003 = -0.48×10^{11} mol
2004 = -13.6×10^{11} mol

2005 = -0.7×10^{11} mol

While the magnitude is relatively small compared to the global flux of 1.3×10^{14} mol, the order of magnitude changes from year to year is much greater than the interannual variability estimated on global scale of less than 20 %.

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Seasonal to Interannual Biogeochemical Variability in the Indian Ocean: The Importance of Inter-regional Connections and their Modulation by Climate Modes

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Recent studies indicate that inter-regional connections are crucially involved as driving mechanisms behind the seasonal to interannual variability in biogeochemical processes observed around the Indian Ocean (IO). These new insights into IO biogeochemical processing have been facilitated by comprehensive oceanographic sampling programs, ongoing accumulation of physical and bio-optical data measured from remote sensing platforms and the application of basin scale physical-biogeochemical models. In situ observations are especially sparse outside of the Arabian Sea and Bay of Bengal. Thus remote sensing data and modeling studies currently offer the primary means of investigating the pelagic system's response to basinwide variability in the physical environment. Evidence of biogeochemical links to regional interconnectivity was apparent in analyses of the Arabian Sea JGOFS observations from the 1990s. The JGOFS data clearly demonstrate that monsoonal forcing drives mesoscale activity and pronounced diurnal mixed layer cycling, both of which are primary determinants of biogeochemical variability in the Arabian Sea. Such regional processes are superimposed on a physical environment that is additionally affected by low frequency atmospheric forcing and remotely forced signals that propagate between regions. The primary inter-regional connections are associated with the semiannual Wyrtki Jet, westward propagating Rossby waves and the northward flowing phase of the Somali Current. To address how these inter-regional connections impact ecosystem variability over the entire IO basin, EOF analyses of remote sensing observations and a fully coupled, 3-D biogeochemical-physical ocean general circulation model are utilized. The ocean model's ecosystem has nine components, consisting of a large and small size class for phytoplankton, zooplankton and detritus, as well as three nutrients (nitrate, ammonium and iron). Results from climatologically forced experiments illustrate biogeochemical variability associated with typical inter-regional connection mechanisms. These typical linkages, and the associated biogeochemical patterns, are significantly disrupted during manifestations of the IO Dipole or Zonal Mode (IODZM). During the 1990s there were three prominent manifestations of the IODZM. EOFs of the available remote sensing data are used to assess an interannually forced model experiment. This interannual solution is then used to provide an initial quantification of how IODZM-driven biogeochemical adjustments impact basinwide fluxes of organic matter.

The Unexpected Impact of Increasing Ocean Acidification on the Production of Dimethyl Sulfide and Other Climate Relevant Organic Gases and Possible Implications to Climate

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Increasing concentrations of atmospheric CO_2 have already elevated ocean surface water pH by 0.1 pH units compared to preindustrial values and pH is expected to decrease an additional 0.3 by the end of this century. Pronounced physiological changes in some marine phytoplankton have been observed during previous CO_2 perturbation experiments. Marine microorganisms are known to consume and produce climate relevant organic gases. Nearly 60 hydrocarbons, halocarbons, alkyl nitrates and organic sulfur trace gases were quantified from sea water samples collected during the Third Pelagic Ecosystem CO_2 Enrichment study (PeECE III) CO_2 perturbation experiment. Three replicate mesocosms of three scenarios representing the present day CO_2 atmospheric concentrations (equilibrated to 375 ppmv of atmospheric CO_2), future CO_2 concentrations anticipated by the end of this century (when considering the IPCC's business as usual scenario, 750 ppmv of CO_2), and a triple present day CO_2 case (1150 ppmv CO_2) were sampled each day over the 24 day experiment. Peak dimethyl sulfide (DMS) concentrations corresponded with the bloom in *Emiliania huxleyi*. The peak in DMS came a few days later in the double and triple CO_2 mesocosms and the time integrated average amount of DMS was 22 and 14 percent higher in the double and triple CO_2 "Worlds", respectively. Chloroiodomethane had its peak concentration much later than the maximum in chlorophyll corresponding to the decline of the phytoplankton bloom. (At this time DMS experienced a secondary maximum.) When integrating the CH_2ClI concentration with respect to time, we estimate that production of CH_2ClI was about 40 percent higher in the $2xCO_2$ and about 140 percent higher in the $3xCO_2$ mesocosms.

Marine production of DMS critically impacts the radiative properties of the Earth because it is a major source of cloud condensation nuclei in the clean marine environment. A significant perturbation to its production and subsequent sea-to-air flux would alter the Earth's albedo. Marine production of CH_2ClI is a source of atmospheric iodine (I). Once released to the atmosphere, atomic I participates in catalytic ozone (O_3) destruction. The concentration of O_3 is pivotal to the oxidative capacity of the atmosphere because it is a primary hydroxyl precursor. Significant future iodine emissions would result in lower O_3 mixing ratios and ultimately lead to longer lifetimes of some greenhouse gases such as methane. Perturbations of these gases, by the few marine microorganisms studied during PeECE III, suggests the potential impact on other marine climate relevant gases as a result of projected ocean acidification.

International Pilot Experiment on CO_2 Mitigation by Disposing Liquid CO_2 Hydrate Into Deep Monterey Bay

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An International Ocean Disposal Experiment was successfully conducted in Monterey Bay. Participants included the Institute of Ocean Sciences (IOS), the Monterey Bay Aquatic Research Institute (MBARI), the Oak Ridge National Laboratory (ORNL), the US Department of Energy (DOE) and Massachusett Institute of Technology (MIT). The MBARI research ship "Western Flyer" and the remote operating vehicle "Tilburon" were used in the experiment. Liquid CO_2 was injected at 1000- 1400 m depth. Above 1000 m, liquid CO_2 rose and decomposed into bubbles. At 1400 m or below, liquid CO_2 reacted with seawater to form a CO_2 hydrate, which sank into deeper waters. The liquid CO_2 hydrate came out of the injector as "spaghetti" which broke up as segments sinking into deep water and settled into the ocean floor. Future disposal experiment will be conducted to understand better the hydrate formation process, to test a faster multi-injection technique also using larger injection tubes, and to investigate the environment impact of CO_2 hydrate on the seafloor biogeochemistry and marine life. The injection process, the CO_2 hydrate formation, and the breaking-up and sinking of the CO_2 hydrate were recorded in a video.

Oceanic Production of Phytoplanktondimethylsulphide: Climate Effect of ENSO on the Upper Ocean.

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Time-series of DMS levels measured between 1996 and 2001 in spring and summer at two offshore stations in the sub-arctic eastern NE Pacific coinciding with an ENSO (El Niñ0-Southern Oscillation) transition. DMS concentrations were 1.5 to 2.5 times higher during the late springs of 1996-98 than that of 1999-2001. Phytoplankton species rich in DMSP (an algae precursor to DMS) were also abundant in 1998 than during 1999-2001 of low DMS. The ENSO event was characterized by warmer, more stratified waters shallowing to about 19 m, from 1996 to 1998, than during the following years. These results provide a first example of how climate fluctuations, through altering the physical and chemical properties of the upper ocean, may influence the structure of the phytoplankton assemblages and hence DMS concentrations in the open ocean.