In particular, the Princeton Ocean Model is adapted to provide a high resolution numerical model of the circulation along Australia's southern shelves as forced by summertime meteorology. The model extends from near Cape Leeuwin in the west to the west coast of Tasmania and the open boundaries are relaxed towards transports obtained from a global circulation model. The primary focus of the study is the slope and shelf circulation within the Great Australian Bight and off the gulfs region of South Australia where upwelling is known to occur.

The dynamics of the circulation is determined to involve several factors including the negative wind stress curl, geostrophic adjustment to the remnants of the wintertime density field and baroclinic instability, the latter leading to the generation of 160km scale eddies over the shelf slope. Paradoxically, winds while upwelling favourable near the coast, drive currents which converge over the shelf break leading to downwelling of 100m or more, and an eastward current which flows in the opposite direction to both the nearshore currents and Flinders current (a northern boundary current) farther offshore. Hydrographic and current meter data is cited to support such a sceanario.

URL: http://www.maths.unsw.edu.au/~jffm

OS32R HC: 319 B Wednesday 1330h

CDOM in the Coastal Ocean: Transformation Processes and Their Effects on Optical Properties III

Presiding: **D G Zika,** University of Miami**; D D Clark,** Chapman University

OS32R-01 1330h

The Role of Seagrasses as a Source of CDOM to Tropical Coastal Waters

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To examine CDOM sources to tropical oligotrophic coastal waters, we conducted a time series study using a moored AC-9, CTD and current meter placed at a site (7-8 m water depth) on the shallow water Bahama Banks. An examination of the data in this 30 hr time series indicated that there were large changes in CDOM absorbance over the tidal cycle, with high dissolved CDOM absorbance being associated with the high salinity waters that originate from the shallow banks. Combining these results with current measurements indicated that there was a net flux of CDOM off the shallow banks to the deeper waters of Exuma Sound. The CDOM spectral slope also varied with the tidal cycle implying that there were differences in the type of CDOM (as well as its absolute amount) being exchanged between deep waters and the shallow banks. Both CDOM absorbance and total DOC showed a positive relationship with salinity, which is opposite of that seen in most coastal systems, in which high DOC and CDOM concentrations are generally associated with low salinity waters of terrestrial origin.

We believe that seagrasses and seagrass sediments represent the most likely sources of this CDOM. Seagrasses are important primary producers in oligotrophic tropical coastal waters and generate a significant amount of the particulate organic matter that settles into the sediments. They also promote the deposition of allocthonous organic matter to seagrass sediments as a result of the leaf canopy altering (dampening) water motion and tidal currents. Consistent with these suggestions, DOC and CDOM levels were significantly higher in the sediment pore waters of vegetated areas versus adjacent bare (ooid) sands. Therefore, we believe that processes associated with seagrass biogeochemistry and decomposition likely represent the predominant mechanisms by which CDOM is input to such oligotrophic tropical coastal waters that experience little or no terrestrial freshwater input.

OS32R-02 1345h

Inputs to and Removals From the Colored Dissolved Organic Matter Pool by the Pelagic Larvacean, *Oikopleura dioica*.

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Oikopleura dioica is a pelagic tunicate that feeds by pumping water through an extruded gelatinous house containing food-concentrating filters with a mesh size of 0.2 μm. *O. dioica* is a common neretic species and has the potential to affect DOM pools by both removing larger colloidal material and by inputting excreted dissolved material. Chromophoric dissolved organic material (CDOM) is a variable but significant component within the total dissolved organic matter (DOM) pool that influences the optical characteristics of the water column. Little is known about *in situ* biological production of CDOM in coastal environments. Laboratory experiments were conducted at the University of Oviedo, Spain to examine the hypothesis that *O. dioica* could influence CDOM pools in coastal environments.

Laboratory experiments were conducted with cultured *Oikopleura dioica* to examine the excretion of chromophoric dissolved organic material and the ingestion of fluorescently labeled fatty acids and dextrans ranging from 400 daltons to 70 kdaltons. Results from these experiments indicate that *O. dioica* does excrete fluorescent protein-material and fluorescent humic-material. Additionally, preliminary results indicate that *O. dioica* is capable of ingesting material as small as 800daltons. Results from these experiments will be discussed in terms of how *O. dioica* can affect the DOM pool and specifically the CDOM pool.

URL: http://www.es.umb.edu/jur/cdom_connection_o_dioica.html

OS32R-03 1400h

A Novel Radioisotopic Technique to Measure Biological Uptake of Dissolved Humic Compounds

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Terrestrially derived colored dissolved organic material (CDOM, eg. humic and fulvic acids) can be an important source of dissolved organic carbon in coastal marine systems. The bioavailability of these compounds has been difficult to measure directly however. A novel technique has been developed to provide radiolabeled humic material for uptake studies. ^{125}Iodine is attached to extracted humic and fulvic material by an iodination reaction catalyzed by lactoperioxidase, with subsequent purification by size-exclusion and ion exchange chromatography. The isotopic signal of the resulting ^{125}I-labeled Suwannee River humic acid exhibited aggregation properties over a range of salinities consistent with that of humic acid. Uptake rates of ^{125}I-labeled humic and fulvic acids by marine bacteria and phytoplankton were quantified under a variety of environmental conditions including 1) prior to and after a significant rainfall event, 2) an onshore offshore transect into the eastern Gulf of Mexico and 3) in phytoplankton culture experiments. Uptake rates of natural populations ranged from 0.0 to 1.4 μg humic acid L^{-1} hr^{-1} and were greatest in the bacterial fractions in all experiments. Uptake by phytoplankton in natural populations did occur however and culture experiments demonstrate that the ability to take up humic compounds is species specific in phytoplankton.

OS32R-04 1415h

Seasonal Variability in the Diurnal Cycling of a Short-lived Photoproduct of CDOM: Spring-Summer Comparison of Carbon Monoxide Time-Series Data at BATS

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In the upper ocean, carbon monoxide (CO) is formed photochemically from CDOM. Its sinks are microbial consumption (major) and gas exchange (variable but minor). Concurrently, mixing redistributes CO within the mixed layer on diurnal and faster scales.

We examine two high-precision, high-resolution time series datasets of near-surface [CO] at BATS in periods of similar insolation and day length but strongly contrasting meteorology (wind speed, E-P), and oceanography (temperature, mixed layer depth and upper thermocline structure, microbial activity; also optics, including [CDOM] and likely CDOM quality).

These differences would a priori be expected to result in very different diurnal cycle patterns (amplitude and shape); paradoxically, this was not observed. Instead, the interplay of production, consumption, outgassing, and mixing somehow usually results in strongly compensatory effects, so that CO near-surface diurnal concentration time-series are quite similar within and between seasons. This "CO cycle buffering" will be explored using constraints from the concurrent process studies. Brief periods with markedly different cycle patterns will be discussed in this light as well.

OS32R-05 1430h

Photo-production of Ammonium from Chromophoric Dissolved Organic Matter (CDOM) in Coastal Waters.

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The role of Chromophoric Dissolved Organic Matter (CDOM) photo-mineralisation processes and the production of inorganic nutrients, have received much increased interest recently. Photo-production of ammonium in aquatic environments is one such process and linear production kinetics have been observed over several hours associated with CDOM-fading. We report here results from a number of irradiation experiments carried out using authentic, filtered river, estuarine and marine water samples. The ammonium production results showed three distinct phases; initially a lag period, followed by production and finally a consumption phase. The lag phase was completed in under 1 hour with maximum concentrations reached in approximately 2 hours, followed by abiotic uptake of ammonium to return concentrations to original levels within 6-24 hours. Estimated production rates were approximately 100 nmoles per litre per hour and showed no relationship to CDOM or salinity, in contrast to previous work. Based on the production rates of ammonium estimated from this work and assuming a mixed layer depth of 50 metres and annual mean global irradiance at 40 degrees latitude, we estimate the potential net photo-release of ammonium to be in the order of 40 Tg per year.

OS32R-06 1445h

The Influence of Copper Speciation on the Photobleaching of CDOM in the Cape Fear Estuary

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The influence of environmentally realistic concentrations of Cu on the photobleaching characteristics of colored dissolved organic matter (CDOM) in the humic rich Cape Fear Estuary was investigated. Concentrations of total copper as low as 20 nM significantly reduced the photobleaching of CDOM relative to controls with no added copper. The photoprotective properties of Cu most likely result from Cus ability to scavenge highly reactive radicals produced during irradiation of estuarine water. When samples were deoxygenated prior to photolysis, the influence of added copper was reduced but not eliminated . This suggests some of the radicals responsible for photobleaching of CDOM are produced in the absence of oxygen. Additional sunlight irradiation experiments demonstrated some fraction of the ligands responsible for organic complexation of copper in the estuary are photochemically labile. The loss in ligand was comparable in magnitude to increases in Cu(I) in irradiated samples suggesting the photodegradation of organic copper complexes results in subsequent production of reduced copper in Cape Fear samples.

OS32R-07 1520h

Photochemical and Biological Degradation of CDOM in Waters from Selected Coastal Regions of the Southeastern United States

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Biological and photochemical degradation of colored dissolved organic matter (CDOM) were investigated in controlled experiments using waters from southeastern U.S. estuaries, from the Mississippi River plume and Gulf of Mexico, and from the coastal shelf region in the Florida Keys. Results of the experiments generally indicated that photoreaction results in decreases in the absorption and fluorescence of terrestrially-derived CDOM as well as CDOM derived from seagrasses. Changes in both absorption spectra (increased spectral slope coefficients) and excitation-emission spectra (hypsochromic shifts) also were observed. Terrestrially-derived CDOM photoreacts to produce biologically-labile photoproducts (BLPs) that were measured using cumulative bacterial oxygen consumption during post irradiation-incubation as an index. The spectral slopes of apparent quantum yield spectra for BLP production were similar to those observed for carbon monoxide production and BLP production rates in sunlight were of the same order of magnitude as those for direct DIC photoproduction. Comparisons of photobleaching and BLP production rates for terrestrially-derived CDOM in the Mississippi River plume on the Gulf of Mexico surface and for algal-derived CDOM in chlorophyll maxima below the surface indicate that these two primary CDOM sources may have quite different photoreactivity. Photobleaching and BLP production for the algal derived CDOM were significantly slower than for the terrestrially-derived CDOM from two sites in the plume west of the mouth of the Mississippi River.

OS32R-08 1535h

Reactions of Hydroxyl Radical (OH) with Chromophoric Dissolved Organic Matter (CDOM): Bleaching and Mineralization

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Photobleaching and photomineralization reactions of chromophoric dissolved organic matter (CDOM) may proceed via two different general pathways: direct photochemical reaction of CDOM following absorption of light, or indirect reaction with photoproduced intermediates such as hydroxyl radical (OH), singlet oxygen ($^1O_2$), superoxide (O_2^-), or, in seawater, dibromide radical (Br_2^-). The balance between these two processes is not well understood. In this study, we examine the role of hydroxyl radical (OH) as a mechanism for the photodecomposition of CDOM. Using gamma-radiolysis of water, OH was generated in several coastal seawater samples, a humic bog water sample, and solutions of standard humic substances in quantities comparable to those produced on time scales of days in sunlit surface waters. The second-order rate coefficients of OH reaction with Suwannee River Fulvic (2.7×10^4 s^{-1} (mg C/l) $^{-1}$) and Humic Acids (1.9×10^4 s^{-1} (mg C/l) $^{-1}$) are comparable to those observed for DOM in natural water samples and DOM isolates from other sources, but decrease slightly with increasing OH doses. OH reactions with humic substances produced dissolved inorganic carbon (DIC) with a high efficiency of 0.3 mol CO_2 per mol OH. This efficiency stayed approximately constant from early phases of oxidation until complete mineralization of the DOM, and was not significantly altered by the addition of 0.1 M Br^-. Bleaching of both humic chromophores by OH and marine CDOM by Br_2^- was relatively slow. Our results indicate that OH reactions with humic substances are not likely to contribute significantly to observed rates of DOM photomineralization in sunlit waters. They are also not likely to be a significant mechanism of photobleaching except in waters with very high OH photoformation rates.

OS32R-09 1550h

Is the Photoproduction of Low Molecular Weight Organic Acids the Primary Mechanism for Increasing the Bioavailability of Dissolved Organic Matter?

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Sunlight has been shown to increase the bacterial availability of dissolved organic matter (DOM) through the formation of readily-available low molecular weight (LMW) substrates. In this study, we use direct measurements of photoproduced LMW organic acids coupled with bioassay experiments to assess the importance of this class of substrates in the photochemical modification of DOM bioavailability. Additionally, several possible mechanisms for the photochemical formation of LMW acids were examined. One of these possibilities, the reaction of photochemically generated hydroxyl radical with DOM, was found to be an insignificant mechanism for the photochemical alteration of DOM bioavailability.

OS32R-10 1605h

On the Nature of the Constituents Underlying the Absorption Spectra of Humic Substances and Chromophoric Dissolved Organic Matter (CDOM)

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The absorption of ultraviolet and visible light by humic substances and CDOM in aquatic environments throughout the world is observed to decrease in an approximately exponential fashion with increasing wavelength. Yet little is known about the light-absorbing constituents responsible for this quite unique wavelength dependence. We have undertaken a series of hole-burning experiments in the attempt to identify the nature and absorption spectra of these constituents. A high intensity narrow-beam Nd-YAG laser pumping a dye laser was employed to destroy selectively chromophores absorbing at specific wavelengths across the UV and visible wavelength regimes. Suwannee River Fulvic Acid and Suwannee River Humic Acid (SRFA and SRHA, respectively) were exposed to monochromatic laser irradiation and the time course of the absorption loss was followed across the entire spectrum. The effect of the reactive oxygen species and secondary photochemistry on the overall photodegradation process was suppressed by working in high viscosity solutions. A series of standards (tryptophan, quinine sulfate, riboflavin and vitamin B12) as well as their mixtures was examined to gain additional insight to this problem. The results obtained from both the standard compounds and the humic substances will be presented.

OS32R-11 1620h

Spatial and Temporal Variation of CDOM Fading Efficiency

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Chromophoric dissolved organic matter (CDOM) loses its ability to absorb radiation after prolonged exposure to sunlight through a process called photobleaching or photochemical fading. Little is known about the efficiency of this process or its variability in the ocean. By irradiating 0.2-um filtered water samples containing CDOM from a wide range of sources (riverine to offshore marine) under a number of sequential long-pass cut-off filters in a solar simulator, we have generated a number of three dimensional apparent quantum yield (3-D AQY) surfaces that quantify the spectral efficiency for CDOM photobleaching. The three dimensions are spectral absorbance, spectral response, and the efficiency of fading.

Measured changes in the spectral absorption of these irradiated samples and the absorption rate of incident energy were used to calculate 3-D AQY surfaces from different locations and through time of exposure using an iterative, nonlinear optimization method that fits the measured CDOM fading to a second order polynomial function. In general, fading efficiency for all samples is highest for radiation absorbed in the UV-B region of sunlight. Our 3-D AQY surfaces will provide constraints for models of addressing CDOM optics in the ocean.

OS32R-12 1635h

Photochemical Fading of CDOM in Florida Bay: Measurements and Models

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Predictive process models that describe the time evolution of ocean optical properties must include a quantitative spectral evaluation of CDOM absorptivity and the photochemically driven loss of that absorptivity (fading). Multi-spectral laboratory determinations of 3-dimensional quantum efficiency surfaces (absorbed wavelength vs. response wavelength vs. efficiency, see Ziolkowski and Miller, this session, for details) for CDOM fading can be generated for this purpose. These fading surfaces, together with solar irradiance and surface layer mixing models, were used to model CDOM fading for conditions found during a cruise in Florida Bay during June 2000. The optical evolution of several drifter-tagged water masses were monitored for up to a week with direct measurements of CDOM and particulate absorbance, and total attenuation of downwelling irradiance (Kd) in the ultraviolet. Comparisons between modeled and measured CDOM UV spectra demonstrate the utility of this approach as a component of a more comprehensive model for coastal ocean optics.