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Variations of size and distribution of the marine sedimentary reservoir of methane in geologic history are increasingly viewed as important for the global carbon cycle. Typically, the evidence for such variations is circumstantial because it is based on stable isotope compositions of calcareous fossils or total organic carbon. We have extended the high-resolution record of distribution and isotopic composition of prokaryotic biomarkers in sediments from the Santa Barbara Basin (SBB), ODP site 893, to two continuous intervals covering the late Pleistocene and early Holocene. The distribution of biomarkers from methanotrophic prokaryotes indicates that concentrations of methane in basin waters have systematically varied in phase with Northern hemispheric climate oscillation. The most plausible source of the methane is sedimentary methane hydrate as proposed earlier [Kennett et al., Science 288, 128-133, 2000]. Previous estimates about rates of methane outgassing will be refined on the basis of molecular data. A complex ecological feedback of surface water communities to conditions prevailing during dissociation of hydrate is indicated by increases in relative abundance and isotopic composition of biomarkers from prokaryotic and eukaryotic algae shortly after or coinciding with the presumed release of methane.

B21B-0732 0830h POSTER

Growing Season Patterns in Eriophorum vaginatum L. Biomass Allocation: the Influence of Experimental Manipulation

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Detailed comprehension of bigeochemical cycling under current and future climate regimes requires a thorough knowledge of root dynamics. With recent improvements in optic and electronic technology, minirhizotron camera systems have become a useful tool for measuring aspects of the belowground dynamic in some natural systems. This study used minirhizotron camera technology during 2001 and 2002 at the Toolik Lake Long Term Ecological Research site in Northern Alaska. Growing season patterns in root production rate and leaf growth rate were examined in the arctic sedge, Eriophorum vaginatum L., under ambient, warmed and fertilized conditions. Experimental results demonstrate a similar response to warming and fertilization. Aboveground, and belowground, plants were physiologically and phenologically plastic in their response. Warmed and fertilized plants exhibited higher leaf growth rates and earlier emergence of the seasons final leaf cohort. Belowground, warmed plants produced roots at a faster rate than plants in control plots, but these high rates were confined to an early- and late-season peak. In fertilized plots, plants responded with just an early season peak in root production rate, but one with rates that exceeded those seen under ambient and warmed conditions. The similarity in warming and fertilization response characteristics may arise independently, or warming and fertilization may act upon the same proximal variable (i.e., plant-available nutrients). Identification of driving variables and the range over which E. vaginatum can capitalize will further our mechanistic understanding of current growing season allocation patterns and facilitate prediction of future species assemblages and interactions.

B21C MCC: 132 Tuesday 0830h

Biogeochemical Cycling of Carbon, Nitrogen, and Heavy Metals: Implications for Ecosystem Restoration and Global Cycles I *(joint with OS)*

Presiding: **J O Sickman,** California Department of Water Resources**; A Mueller-Solger,** California Department of Water Resources

B21C-01 0830h INVITED

The Contribution of Natural and Restored Wetlands to Changes in the Concentration and Composition of Dissolved Organic Material in the Sacramento-San Joaquin Delta and San Francisco Estuary

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The quantity and quality of wetland-derived dissolved organic material (DOM) entering delta and estuary environments remains poorly characterized, even though DOM has two roles of societal significance: 1) it supports estuarine foodwebs, which commonly are a habitat for endangered species, and 2) it presents problems when it occurs in drinking water supplies, because it forms carcinogenic byproducts when treated. The Sacramento-San Joaquin Delta is a source of drinking water for more than 20 million people and contributes 80% of the DOM entering the San Francisco estuary, nearly doubling the concentration of DOM in the influent river water. The majority of the Delta is composed of below-sea-level peat islands that are maintained in agricultural production by continuous pumping of DOM-rich drain water into Delta channels. Previous studies indicate that changes in DOM composition in water passing through the Delta are not consistent with the addition of peat island drain water, and are more consistent with the addition of wetland-derived material. Therefore, wetlands may contribute substantially to DOM export to the estuary. Although wetlands currently constitute only 14% of the Delta, restoration is planned that would more than double this wetland area, potentially altering DOM quality and content in the Delta and estuary waters. During the past several years, the seasonal variation in the quality of DOM added by a variety of wetland types and island drains within the Delta and estuary has been examined. In this study, 13 sites were sampled 5 times. As of September 2002, the samples have been analyzed to determine the content of hydrophobic DOM, characterize the ultraviolet absorbance and fluorescence properties, and quantify the susceptibility to biodegradation before and after photoexposure. Samples were humic-rich, averaging more than 75% hydrophobic content and varying from 74 to 86%, with the variation in hydrophobic content between samples corresponding to changes in the optical properties. Samples typically were refractory with respect to biodegradation, having an average of 11% of the DOM being susceptible to biodegradation prior to photoexposure, but the range was from 1% to 48%. Following photoexposure, samples generally were more refractory rather than more labile. Wetland DOM reacted to form more drinking water disinfection byproducts than influent waters, but some wetland types seemed to contribute fewer precursors. Seasonal variation in biodegradation and chemical parameters was much greater than variation among wetland types, and the peak of biodegradability was not related to the seasonal peak in DOM. Therefore, the addition of DOM through the Delta is controlled by changes in the nature of the source material rather than changes in efficiency or extent of remineralization.

B21C-02 0845h INVITED

Watershed nutrient inputs, phytoplankton accumulation, and C stocks in Chesapeake Bay

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Inputs of N and P to Chesapeake Bay have been enhanced by anthropogenic activities. Fertilizers, urbanization, N emissions, and industrial effluents contribute to point and diffuse sources currently 2-7X higher for P and 5-20X higher for N than those from undisturbed watersheds. Enhanced nutrient inputs cause phytoplankton blooms which obscure visibility, eliminate submerged grasses, and influence the distribution of C within the Bay. Accumulations of dissolved organic and particulate organic C lead to enhanced microbial respiration in isolated bottom waters, and dissolved oxygen is seasonally reduced to trace levels during summer.

Cultural eutrophication is not unique to Chesapeake Bay. Although some estuaries such as the Delaware, Hudson, and San Francisco Bay also have high anthropogenic inputs, these estuaries have much shorter residence times, and much of the N and P may be exported to the coastal ocean. However, in Chesapeake Bay, with residence times > 2 months, internal processing of watershed inputs results in local algal blooms within the estuary.

Watershed restoration strategies for Chesapeake watersheds have had limited success to date. Groundwaters are enriched with nitrate, and the long residence times of groundwaters mean slow responses to watershed improvements. The few successes in the Chesapeake have been associated with point source reductions, although continued human population growth can easily override restoration efforts. Widespread improvement in water quality has yet to occur, but the limited successes show that the Bay responds to load changes.

B21C-03 0900h INVITED

Ecosystem Modulation of Dissolved Carbon Age in a Temperate Marsh-Dominated Estuary

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The concentrations and isotopic values (Δ14C and δ13C) of dissolved inorganic, organic and particulate organic carbon (DIC, DOC, and POC, respectively) were measured in the Parker River watershed and its associated estuary to determine the age of carbon entering the estuary and how estuarine processing affects the quantity and apparent age of carbon transported to the Gulf of Maine. The watershed measurements indicated the transport of Δ14C-enriched modern DIC and DOC and variably aged POC from the watershed to the estuary. Surveys within the watershed aimed at determining which land use type dominated the DOC export indicated that wetlands, although making up 20% of the land use could be responsible for 75% of the DOC export. We therefore conclude that the wetland land uses of the Parker River watershed are exporting mainly D14C-enriched modern DOC. DIC isotopes indicate that the source of DIC in the Parker River watershed is dominated by the weathering of non-carbonate parent material by /Delta14C enriched CO2 originating from the respiration of young organic matter in soils.

Transects in the associated estuary displayed net additions of all carbon species. For DOC and DIC the fluvial export of this internally added DOC and DIC was approximately equal to the amount being exported from the watershed, stressing the importance of focusing on estuaries when estimating the export of carbon to the coastal ocean. With respect to DIC, the total input is even larger when the atmospheric exchange of excess pCO2 is calculated. The /Delta C-DOC and /DeltaC-DIC transects both indicate that the internally added DOC and DIC is /DeltaC-enriched modern material. The source of this material is the associated marshes and estuarine phytoplankton, with the relative

importance of these two sources changing from transect to transect. Coupled together, the bulk carbon and /DeltaC measurements show that the estuary is adding significant quantities of young DOC despite the existence of vast quantities of old marsh peat flanking the entire estuary. Furthermore, the DIC data indicate that /DeltaC-enriched modern material is also what is fueling the majority of heterotrophic respiration within the system.

B21C-04 0915h

Interactions Between Dissolved Organic Matter and Mercury in the Florida Everglades

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Interactions of mercury (Hg) with dissolved organic matter (DOM) play important roles in controlling reactivity, bioavailability and transport of Hg in aquatic systems. To better define the nature and magnitude of these interactions, experiments were designed using organic matter isolated from various surface waters in the Florida Everglades to determine Hg-DOM binding constants and to study the interactions between DOM and cinnabar (HgS). The isolates, obtained using XAD resins, exhibited a wide range of elemental compositions, aromatic carbon contents, reduced sulfur contents, and molecular weights. Chemical composition of the DOM, especially aromatic carbon and reduced sulfur functional group content, was found to be important in controlling DOM interactions with Hg(II).

Conditional distribution coefficients ($K_{DOM'}$), measured using an equilibrium dialysis ligand exchange method, were strongly affected by the Hg/DOM concentration ratio. Very strong interactions ($K_{DOM'} = 10^{23.2}$ L kg^{-1} at pH = 7.0 and I = 0.1), indicative of Hg-thiol bonds, were observed at Hg/DOM ratios below approximately 1 μg Hg per mg DOM. Hg/DOM ratios above approximately 10 μg Hg per mg DOM gave much lower $K_{DOM'}$ values ($10^{10.7}$L kg^{-1} at pH 4.9 to 5.6 and I = 0.1), consistent with Hg binding mainly to oxygen functional groups. These results suggest that the binding of Hg to DOM under natural conditions (very low Hg/DOM ratios) is controlled by a small fraction of DOM molecules containing reactive thiol functional groups.

DOM-Hg interactions were also studied by HgS (log K_{sp} = -52.4) dissolution and precipitation experiments. In the dissolution experiments, a significant amount of Hg was released from cinnabar in the presence of DOM, suggesting strong interactions. Conversely, precipitation of metacinnabar (black HgS) was strongly inhibited in the presence of low concentrations (<3 mg C/L) of DOM. In both the dissolution and precipitation experiments, organic matter rich in aromatic moieties was more reactive with HgS than less aromatic fractions and model compounds. These results suggest that DOM can influence the geochemistry and bioavailability of inorganic complexes of Hg in the Everglades, especially HgS, by strong Hg-DOM binding and colloidal stabilization.

B21C-05 0930h

Effects of Human Activities on the Composition of Organic Carbon in Estuaries: Insights Gained Through Lipid Biomarker Studies

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Applications of organic geochemistry have expanded in recent decades to include studies within fields as diverse as ecology and ecosystem science, biogeochemistry, and environmental geochemistry. In part, this expansion has occurred in response to increasing human impacts on the environment which are manifested to a large extent in freshwater and estuarine environments. Human influences to these regions include alterations in carbon and nutrient flow, changes in sedimentation and the introduction of industrial and petroleum products. Organic geochemists bring new tools and insights to these areas improving our ability to trace specific components of organic matter. These approaches have the capacity to improve our understanding of the role nearshore regions play in the global carbon cycle, better identification of the sources and mode of delivery of natural and anthropogenic organic molecules, and an improved understanding of the fate of organic molecules including remineralization, transformation, or burial in sediments. Chesapeake Bay and San Francisco Bay are the largest estuaries in the continental U.S.A. and provide an interesting comparison for understanding processes influencing the composition of estuarine particulate organic matter (POM). Both estuaries have also been heavily impacted by human activities thus providing an opportunity to investigate how anthropogenic activities influence POM quantity and quality. Results from biomarker analysis of suspended POM and surficial sediments collected from each estuary will be presented and summarized in this talk. Stable isotopic signatures and lipid biomarker compounds reveal spatial variations in organic matter sources along the salinity continuum of each estuary with a stronger terrigeneous signature at the freshwater end-member. In addition, temporal variations in freshwater inflow and phytoplankton production influenced the sources and reactivity of POM. This talk will demonstrate that results from biomarker studies provide insights more useful to the restoration and rehabilitation of estuaries than bulk measurements alone. I will also present examples of how biomarker applications can also be used to provide insights regarding changes in organic carbon inputs over historical and geological timescales. In the future, resource managers and policy makers should consider both the amount of carbon produced within each system as well as its composition and source. These parameters influence OM availability to heterotrophic organisms and determine whether a system is likely able to support production at higher trophic levels.

B21C-06 0945h

Carbon Dynamics Change Over Time in a Restored Freshwater Wetland in the Sacramento- San Joaquin Delta, California

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While gaseous carbon (C) losses from a restored freshwater wetland increased during the period from 1997 to 2002, mass loss of litter decreased over time in sequential litterbag decomposition studies. Previously farmed organic soils on Twitchell Island were flooded to two water depths to assess the use of continuous shallow flooding of peat soils to mitigate subsidence in the Sacramento-San Joaquin Delta, California. Compared to a neighboring agricultural field, flooding in the study field reduced total gaseous C losses by as much as one order of magnitude, though methane emissions were higher during. Increases in carbon dioxide emissions corresponded to increased colonization of emergent marsh plants. Decomposition of new litter inputs was examined using litterbags containing senesced shoots of two dominant freshwater marsh plants, cattails (Typha) and tules (Scirpus). Litterbag decomposition studies were initiated in November 1997, February 1999, and May 2000, and each continued for at least 2 years. These studies compared the effects of plant species, water depth, location in the water column on mass loss of litter, and C and nitrogen contents. While the treatment factors affected litter decomposition for each study, these factors did not affect the decreases in the extent of decomposition when consecutive studies were compared, regardless of individual treatments. Thus, total litter loss decreased as the wetland matured. Depending on plant species and litter location, mass loss of litter ranged from approximately 85 to 95% of inputs from November 1997 to January 2000; from approximately 60 to 85% of inputs from February 1999 to March 2001; and from approximately 60 to 75% of inputs from May 2000 to September 2002. These changes in mass loss of litter during marsh development could have a great effect on estimates of C storage potential of these wetlands in the Sacramento-San Joaquin Delta.

B21D MCC: 130 Tuesday 0830h

The Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA) I *(joint with A, H)*

Presiding: **C Nobre,** Centro de Previsão de Tempo e Estuidos Climáticos (CPTEC)**; M Keller,** University of New Hampshire

B21D-01 0830h

Changes in CO_2, N_2O and NO Emissions in Response to Conventional Tillage and No-tillage Management Practices in the State of Rondonia, Brazil

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Land management in the Brazilian State of Rondonia is undergoing a new phase at the start of 21st century. In the 1970s and afterwards, vast tracts of tropical forest were cleared and planted to pasture for cattle grazing. With decades of use, the productivity of these pastures has declined. Now, in an effort to restore productivity, new land management regimes are being implemented that involve either tillage or no-tillage options combined with various combinations of fertilizer application, herbicide use and the planting of a cash crop prior to the planting of forage grasses.

We are studying a subset of these restoration practices in a large-scale (>3 ha), replicated field experiment in an area of degraded pasture at Fazenda Nova Vida, a 22,000 ha cattle ranch in central Rondonia. Here we report on the emissions of carbon dioxide (CO_2), nitrous oxide (N_2O) and nitric oxide (NO) from the initial phases (first six months) of three of the treatments. The treatments are - 1) control; 2) conventional tillage followed by planting of forage grass (Brachiaria brizantha) and fertilizer additions; 3) no-tillage/herbicide treatment followed by two plantings, the first being a cash crop of rice followed by forage grass. In treatment 3, the rice was fertilized.

Relative to the control, tillage increased CO_2 emission by 37% over the first two months, while the no-tillage/herbicide regime decreased CO_2 emissions by 7% over the same period. The cumulative N_2O emissions over the first two months from the tillage regime (0.94 kg N ha^{-1}) were much higher than the N_2O releases from either the no-tillage/herbicide regime (0.64 kg N ha^{-1}) or the control treatment (0.04 kg N ha-1). The highest levels of N_2O fluxes from both management regimes were observed following nitrogen fertilizations. The cumulative NO releases over the first two months were largest in the tillage treatment (0.98 kg N ha^{-1}), intermediate in the no-tillage treatment (0.72 kg N ha^{-1}), and smallest in the control treatment (0.12 kg N ha^{-1}). For the first week following fertilization the percentage of fertilizer N lost as N_2O plus NO was 1.0% for the tillage treatment and 3.0% for the no-tillage treatment.

Because pasture restoration will continue in Rondnia and other parts of the Amazon Basin, we can expect changes in CO_2, N_2O and NO emissions to the atmosphere from the region. For CO_2, both the sign and magnitude of these changes will depend on the restoration regime chosen. Nitrogen oxide emission will increase as the rate of pasture restoration increases with the magnitude of the increases being restoration-regime dependent.

B21D-02 0845h

Regionalization of Methane Emissions in the Amazon Basin with Multi-temporal Microwave Remote Sensing

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