### OS12G-09 1550h

#### Chemical Characterization and Bioavailability of Dissolved Organic Matter using Atmospheric Pressure Electrospray Ionization Mass Spectrometry

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Dissolved organic matter (DOM) is a complex mixture of organic compounds and is an important source of C and N to rivers and estuaries. As such, DOM can fuel bacterial metabolism, but the reactivity of DOM varies by source and season. Until recently, our understanding of DOM reactivity and bioavailability has been limited to bulk-level analyses or to some specific fraction of the DOM pool. We present new results using Atmospheric Pressure Electrospray Ionization Mass spectrometry to characterize the bioavailabilty of DOM from various sources. This analytical technique provides information on molecular weight, abundance and acid/base properties. We demonstrate differences in the reactivity of individual compounds and chemically characterize the bioavailable and refractory pools of DOM before and after microbial degradation. Samples from a variety of aquatic sources (forested, agricultural and urban) had different molecular weight distributions or 'fingerprints', as well as different degrees of bioavailability. In an experiment with urban stormwater, approximately 40% of the DOM compounds were bioavailable, and almost all of the available compounds exhibited similar chemical characteristics. This approach has extended our understanding of DOM processing in aquatic systems by providing molecular-level information on the previously uncharacterized complex mixture of DOM compounds.

### OS12G-10 1605h

#### Techniques for the Analysis of Intact Protein in Marine Sediments

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Proteins represent the largest biochemical class of compounds identified in marine sediments. Traditional thought suggested that proteins were very labile, and therefore unable to withstand diagenetic transport and alterations. The majority of studies to date on sedimentary protein concentrations and dynamics have relied on the analysis of protein subunits, i.e. amino acids or peptide bonds. This has limited, or eliminated, all information on the size, type and source of the protein or peptide along with any sequence information. The primary focus of our research has been to develop techniques to look at intact proteins and peptides in sweater, sediments, and pore water. Recent advances in proteometrics now allow for a higher tolerance for salts and impurities from biological matrices and also permit greater sensitivity for protein analysis. With the development and use of LC-ESI-MS-MS and MALDI-TOF-MS systems we are able to observe cleavage patterns of known proteins by natural bacterial assemblages. Most recently, we have also extracted and analyzed naturally occurring proteins from sediments and seawater from the Washington coast. Results to date indicate a predominance of extractable protein in the mid-size range of 30kDa.

### OS12G-11 1620h

#### The Application of Electrospray Ionization FT-ICR Mass Spectrometry to the Study of Natural Organic Matter

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Molecular level characterization of natural organic matter has been elusive due to the inherent complexity of natural organic mixtures and the fact that individual components are polar and macromolecular. Electrospray ionization (ESI) is a "soft" ionization technique that ionizes polar compounds from aqueous solutions prior to acceleration into a mass spectrometer. In this study, we have combined ESI with an ultra-high-resolution mass spectrometer, the Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS), to examine individual molecules within a variety of natural organic mixtures. With the high resolution of the FT-ICR MS (<1 ppm error in mass accuracy), we have been able to resolve >9,000 compounds within the 300-1000 Da mass range. At low m/z, the resolution is high enough to assign exact molecular formulas allowing specific components of these mixtures to be identified. In addition to molecular identification, we can now use ESI FT-ICR MS to examine molecular-level changes in different organic mixtures as a function of relevant geo-processes, such as microbial alterations and photochemistry. In this presentation, we will highlight the capabilities of the instrument by showing molecular-level resolution mass spectra of different organic mixtures such as humic substances, riverine DOM and bacterial exudates. In addition, we will present an example of the potential of this technique for molecular-level comparisons as a function of photochemical alteration of riverine DOM.

### OS12G-12 1635h

#### Development of a High Specificity ELISA Assay to Trace the Source and Fate of Biopolymers in the DOC Pool.

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Dissolved organic carbon (DOC) is the largest pool of active organic carbon on earth. Understanding the cycling of DOC is crucial to predict ocean processes ranging from food web dynamics to climate change. To investigate the complex degradation dynamics taking place in the water column it is critical to develop probes of high sensitivity and specificity that can identify the source and trace the fate of specific moieties found in DOC. The unicellular alga Phaeocystis (Prymnesiophyte) is a leading contributor of biopolymers to the dissolved organic carbon pool (DOC). During spring, subpolar and polar oceans blooms of Phaeocystis release huge masses of polymer gels. Most of this material is partially processed by bacteria and other microbial species. However, the final fait of the bulk of Phaeocystis primary production remains uncertain, and the contribution of Phaeocystis polymeric material to the global DOM pool is unknown. We developed an ELISA assay (enzyme linked immunosorbent assay) to quantify the concentration and contribution of Phaeocystis extracellular polymers to the global DOC pool. The concentration of Phaeocystis polymer found in field samples of DOM taken from the Ross Sea, the North Water Polynia and the Gulf of Alaska can range from 0.33 uM to 20 uM carbon. Our results indicate that ELISA provides a powerful highly specific method with nanomolar sensitivity to identify and measure the complex moieties found in DOM. (Supported by grants from the US DOE-BIOMP Program and NSF Division of Bioengineering Biocomplexity Program)

## OS12H HC: 314 Monday 1330h

### Interactions Between Macro- and Microorganisms in Aquatic Sediments II

*Presiding:* **R Haese,** Utrecht University**; J Kostka,** Florida State University

### OS12H-01 1330h

#### Interactions Between the Cold Seep Tubeworm, Lamellibrachia cf luymesi, and interstitial Sulfate Reducing Bacteria: A Perpetual Motion Machine?

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Lamellibrachia cf luymesi is similar to its hydrothermal vent relatives in that it has no mouth, gut or anus and obtains its nutrition from symbiotic chemoautotrophic sulfide-oxidizing bacteria. Also like its vent relatives, L. luymesi supplies sulfide to its symbionts using special hemoglobins in its vascular and coelomic fluids that have a very high affinity and capacity to bind and carry sulfide. However, unlike the well-studied East Pacific Rise hydrothermal-vent tubeworms, adult L. luymesi live in an environment where sulfide is normally not detectable around its gas exchange organ, the obturacular plume. We have recently demonstrated that under some conditions a posterior extension of the worms, nicknamed a root, is capable of taking up sulfide at rates sufficient to fuel net inorganic carbon uptake, or in other words, autotrophy. We have also found that very high (millimolar) levels of sulfide are often present deep in the sediment, around the buried posterior ends of the worms.

Where does this sulfide come from and how is it replenished? It is unlikely to come from deep sources as the oil reserves in this region of the Gulf do not contain sulfide. Furthermore, these pools are present at greater depths than can be explained by diffusion and reduction of seawater sulfate. We will present a hypothesis for a mechanism to deliver the high sulfide flux necessary to supply the roots of the tubeworm aggregations in the Gulf of Mexico, current evidence supporting this hypothesis, and the results of models that constrain the flux of sulfide required by the aggregations and the volume of sediment that supplies this sulfide.

### OS12H-02 1345h

#### Comparison of Clambed and Microbial Mat Habitats at Eel River Methane Seeps, Northern California Margin: Microbiological, Geochemical and Biological interactions

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During 2 cruises (2000 and 2001) we investigated the methane seeps in the Eel River Basin on the northern California margin (500 m). The study area was characterized by 2-m to 10-m patches of bacterial mats and clambeds occurring in close proximity to each other. Our combined studies focused on the microbial processes and resulting geochemical gradients and their role in structuring the different benthic assemblages. We measured concentration profiles using microelectrodes (oxygen, sulfide), applied conventional chemical methods (sulfate, methane), and carried out in-situ

sulfate reduction and methane oxidation rate measurements. Total cell numbers and biomass of methane consuming bacteria were compared in the two habitats. Identification of methane oxidizing consortia using FISH (Fluorescent in-situ hybridization) is planned. Macrofaunal composition and distribution were examined along the chemical gradients with a focus on oxygen and sulfide concentrations. While biological studies at methane seeps have mainly concentrated on sediment surface communities, our investigations also included the infauna organisms.

Clambeds and bacterial mats exhibited striking differences not only in methane concentrations but also in the stable isotopic signature of methane (up to 20 per mil) as well as in the intensity and vertical distribution of sulfate reduction and methane oxidation rates within the sediments. Phylogenetic studies are under way to find out if this difference is also reflected in the microbial diversity. Sulfide concentrations were extremely high (10 - 15 mM) within the bacterial mats, even in the top centimeters. In comparison, the values in the clam beds were much lower and concentration peaked (2 mM) in the zone of highest sulfate reduction. No macrofaunal taxa tolerated the highest sulfide concentrations of 10 - 15 mM: most of the seep infauna were sulfide intolerant. However, a complex of dorvelleid polychaete species tolerated sulfide to concentrations of 1 - 5 mM, as did microbial mats composed of filamentous sulfur oxidizing bacteria.

The extreme conditions characteristic of methane seep sediments are likely to yield new understanding of the interaction of microbial processes, geochemical gradients and benthic assemblages.

### OS12H-03 1400h

## Importance of Benthic Nutrient Regeneration for the Initiation of Macroalgal Blooms in Shallow Embayments

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Despite remedies to counteract eutrophication in coastal marine ecosystems in Sweden, the problem with floating macroalgal mats in embayments still remains. The reason may be that shallow embayments, due to nutrient loading of sediments during recent decades, now function as self-regenerating systems, favouring the growth of opportunistic macroalgae. The role of sediment biogeochemistry for inorganic nutrient efflux was studied in two bays during the pre-bloom and initial growth period of green algal mats. Sediment/water nutrient fluxes were measured, in situ and in the laboratory, together with denitrification, primary productivity, sediment nutrient profiles, and microphytobenthic and faunal biomass and composition. The sediment pool of inorganic nutrients could, depending on site, meet the entire N demand and up to 70 per cent of the P demand of the initial green-algal growth. The availability of this nutrient pool was, however, influenced by the functional type of infauna, and competition by microphytobenthos. The net efflux of inorganic N and removal of N by denitrification were within the same magnitude. The conclusion is that sediment nutrient efflux alone can be sufficient to initiate the growth of algal mats, implying that a delayed effect of decreased nutrient load to the coastal zone can be expected.

### OS12H-04 1415h

## Density-Dependent Impacts of Bioirrigation by the Burrowing Shrimp *Upogebia pugettensis* on Benthic Fluxes and Porewater Solute Distributions in Pacific Northwest Estuaries

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Burrowing thalassinid shrimp are major ecosystem engineering species of Pacific estuaries and can structure the physical, chemical, and biotic properties of sediments. Feeding and burrow irrigation by benthic organisms can increase the remineralization rates of organic material (OM) and the interfacial solute fluxes. This study utilized a combination of benthic chambers and porewater peepers to quantify the role of *Upogebia pugettensis* population density on benthic fluxes and porewater solute distributions in Yaquina Bay, Oregon.

Sediment oxygen uptake was 3-7 times greater in the presence of shrimp and increased linearly with shrimp burrow density ($R^2 = 0.8$). Similarly, the Dissolved Inorganic Nitrogen (DIN = ammonium and nitrate) flux from sediments to overlying water increased with burrow density ($R^2 = 0.66$). At mid and high shrimp densities (55 and 130 burrows 0.25 $m^{-2}$, respectively), nitrate became proportionally more important to DIN efflux from the sediments indicating a potential density-dependent increase in nitrification. *U. pugettensis* also affected porewater solute profiles to $\sim$ 50 cm. The inventory of $PO_4$ and $NH_4$ was inversely related to burrow density with the greatest impact seen in $PO_4$ where integrated concentrations were 8 times greater in no shrimp habitat compared to areas with high shrimp densities. Ammonium and phosphate porewater profiles were most affected by mid- and high densities of shrimp burrows where there was lower solute concentrations in the top 30 cm of the sediment column, presumably due to bioirrigation. In contrast, the solute profiles in the low density (20 burrows 0.25 $m^{-2}$) and no shrimp areas were dominated primarily by diffusive transport.

Thus, populations of *U. pugettensis* have a significant impact on OM and nutrient cycling in Yaquina Bay, which implies an important role for burrowing shrimp in the biogeochemistry of Pacific Northwest estuaries.

### OS12H-05 1430h

## The Role of Bioturbation in Benthic Nutrient Dynamics and Sediment-Water Interface Exchange.

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The contribution of regenerated sources of nutrients from benthic systems has been paid little attention. Trawl disturbances to the seabed potentially cause a wide range of impacts that can modify the assemblage of benthic organisms. Alterations to benthic community structure are likely to have geochemical consequences. Mortality due to trawling is size dependant within and between species, and can effectively cause a shift from large, slow reproducing species to smaller organisms with high turnover rates in those areas subject to repeated benthic disturbance. As bioturbation activity (the natural reworking of sediment by organisms) is positively correlated to body size, the concomitant effects of this could cause significant impacts on the transformations of organic matter by bacteria and the regeneration of, and sediment-water fluxes of, nutrients. This study investigates the role of benthic fauna in modifying the sediment-water fluxes of nutrients in a number of controlled mesocosm experiments. Replicate mesocosms containing five separate treatments were set up. These included; 1, Molecular diffusion controls. 2, Untrawled sediment fauna (Larger organisms). 3, Trawled sediment fauna (Smaller organisms). 4, Density manipulated fauna (To isolate organism interactions). 5, Disturbed sediment systems (Trawl mimicked). Following a stabilisation period the sediment was incubated under flux chambers for 40 hours to determine nutrient concentrations at regular intervals. Based on these measurements benthic-pelagic nutrient fluxes were calculated. Biogeochemical consequences of altered macro benthic interactions are discussed and evaluated.

### OS12H-06 1445h

## Vertical Distribution of Denitrification Rates in Intertidal Sediments

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Denitrification plays a key role in organic carbon mineralization and nitrogen removal in estuarine sediments. The vertical variation in denitrification rates was determined at two different sites in the Scheldt estuary (Belgium, The Netherlands), using two different methods. Microsensors were used to record $N_2O$ profiles in the presence of the $N_2O$ reductase inhibitor acetylene; the actual *in situ* as well as potential denitrification rates were obtained. This method allows a high spatial resolution with negligible disturbance of the sediment. Additionally, intact sediment plugs of 1 cm, from 4 different depths were incubated in flow-through reactors to determine denitrification rates. This method has a lower resolution than the microprofiling, but in addition to nitrate reduction rates, kinetic parameters like $K_s$ and $R_m$ can be calculated. Highest denitrification rates, on average 300 $\mu MNh^{-1}$ by microprofing and 400 $\mu MNh^{-1}$ by plug flow-through reactor, were found in fresh water sediment. In the brackish sediment rates were lower being on average 100 $\mu MNh^{-1}$ determined by plug flow-through reactor incubation. Unexpectedly, high denitrifying activity was determined at depths were oxygen, as well as nitrate, were found depleted by classical pore water analysis and microprofiling. This indicates supply of nitrate at deeper depth, either due to microbial activity, bioirrigation or frequent physical mixing of the top sediment layers. Due to the high abundance of oligochaetes we suspect that bioirrigation is the process responsible for supply of nitrate and oxygen at deeper depths, thus sustaining active denitrification. The combination of the two methods, allowing fine-scaled resolution or determining kinetic parameters, seems promising in predicting denitrifying reaction rates in response to environmental variables (e.g. salinity, carbon, nitrate) and in intertidal sediments.

MON

# OS12I HC: 317 B Monday 1330h

## Synthesis of the Arabian Sea Expeditions III

***Presiding:*** **S L Smith,** University of Miami**; P Burkill,** Plymouth Marine Laboratory**; S W Naqvi,** National Institute of Oceanography

### OS12I-01 1330h

## The "North Arabian Sea High Salinity Water" annually ventilates the upper part of the pycnocline north of 21-22N

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The salinity maximum in the northern Arabian Sea poleward of 21-22oN in the pycnocline at or slightly deeper than the 25 g dm-3 isopycnal, which KB had mentioned in 1968 and described in 1984, is being revisited, principally based on seasonal coverage along five sections each between May 1975 and August 1976. Geographically this "Northern Arabian Sea High Salinity Water" (NASHSW) replaces the Arabian Sea High Salinity Water (ASHSW) of several authors, which is present in the central and eastern Arabian Sea at about 24 g dm-3. Convection appears to renew the NASHSW during each winter at least partially. It ventilates the permanent pycnocline to 150 m or slightly deeper, analogous to the subduction of high-salinity water near the subtropical convergences of the principal oceans.

In the very top of the pycnocline, above the salinity maximum formed by the NASHSW, a thin (decameters) salinity minimum usually occurs, which in one-third of the observed pairs of samples is less well aerated than the first depth of the NASHSW below. Its origin cannot be ascertained, but based on T-S relations, advection and subduction from the east after the close of the NE Monsoon (surface low-salinity water spreading along the west coast of India) and from the southwest (upwelling off Oman due to the SW Monsoon) are possible. The often low oxygen content, though, is puzzling (median saturation of 18 cruise x section medians is 52%, range 20-85% after, omitting a few full-saturation values).

The salinity maximum, occasionally accompanied by the overlying salinity minimum, was found at and above about 22oN in all years with data (1961, 1965, 1966-68, 1974, 1975/76, 1986, 1987, and 1992-1994 [here, with few occurrences among 20-25 offshore stations during each of four cruises]), but not in 1995. It was also observed east of 60oE, at about 20oN and further south in 1986 and 1987, but not during 1965 and 1994/95.