

Aas, P., M. M. Lyons, et al. (1996). "Inhibition of bacterial activities by solar radiation in nearshore waters and the Gulf of Mexico." Aquatic Microbial Ecology **11**(3): 229-238.

The effects of ultraviolet (UV) radiation on thymidine and leucine incorporation were examined in surface waters from the Gulf of Mexico and Santa Rosa Sound, a mesotrophic estuary in northwest Florida, USA. Whole and 0.8 μm filtered surface waters were incubated with H-3-thymidine and C-14-leucine in UV transparent containers under natural solar radiation. Solar radiation was either not filtered (samples exposed to UV-B, UV-A, and photosynthetically active radiation, PAR), filtered through Mylar 500D (samples exposed to UV-A and PAR), or filtered through Acrylite OP3 (samples exposed only to PAR). In Santa Rosa Sound, thymidine incorporation was inhibited an average of 44% relative to dark controls when exposed to unfiltered solar radiation. PAR contributed 23% to the total thymidine inhibition, while UV-A and UV-B contributed 37% and 39%, respectively, to total inhibition. Leucine incorporation in Santa Rosa Sound was inhibited 29% by full solar radiation. The majority of the total leucine inhibition was due to UV-B (83%), while PAR only treatments showed leucine incorporation rates 10% higher than dark controls. For the Gulf of Mexico experiments, full solar radiation inhibited thymidine incorporation approximately twice as much as leucine incorporation. However, there were no consistent patterns in differences due to different wavelengths. Both thymidine and leucine incorporation were inhibited to a greater extent in <0.8 μm filtered water samples than in whole water samples, suggesting that the presence of primary producers may mediate the detrimental effects of solar radiation on bacterioplankton. Surface water was also incubated in situ with thymidine at fixed depths in UV transparent and darkened containers at 3 locations in the Gulf of Mexico. Total inhibition was 60 to 70% at the surface and was evident to 15 m. Comparison with radiometric data and DNA dosimeters indicated that UV-B exerted the greatest effect in the upper 5 m while below that the inhibition was most likely due to longer wavelengths. Our results suggest that both UV and visible solar radiation can negatively affect bacterial metabolism and failure to take into account the effects of light may result in the overestimation of bacterioplankton production in surface waters.

Abrajano, T. A., D. E. Murphy, et al. (1994). "C-13 C-12 RATIOS IN INDIVIDUAL FATTY-ACIDS OF MARINE MYTILIDS WITH AND WITHOUT BACTERIAL SYMBIONTS." Organic Geochemistry **21**(6-7): 611-617.

No evidence was found for isotopic fractionation at methyl carbon during methylation of fatty acids with BF₃-methanol. It is therefore possible to evaluate intermolecular carbon isotopic variations in natural fatty acids by determining the delta C-13 composition of the corresponding methyl esters after derivatization. We illustrate the usefulness of the technique to the evaluation of dietary strategies of marine mytilids in two contrasting marine environments, a normal coastal Newfoundland estuarine system and a cold hydrocarbon seep benthic community from the Gulf of Mexico. Mussels from coastal Newfoundland have fatty acid delta C-13 compositions of -34.4 to -24.9 parts per thousand, whereas those from the Gulf of Mexico showed a range of -56.9 to -49.0 parts per

thousand. This difference is primarily ascribed to the difference in the ultimate source of C1 carbon in the two environments (CO₂ in coastal Newfoundland and CH₄ in the Gulf of Mexico). Differences observed in the nature of intermolecular carbon isotopic patterns of saturated and unsaturated fatty acids of mytilids from the two marine localities reflect the differences in the carbon pathways utilized by the organisms in their respective growth environments.

Aharon, P., E. R. Graber, et al. (1992). "DISSOLVED CARBON AND DELTA-C-13 ANOMALIES IN THE WATER COLUMN CAUSED BY HYDROCARBON SEEPS ON THE NORTHWESTERN GULF OF MEXICO SLOPE." Geo-Marine Letters **12**(1): 33-40. Alkalinity, dissolved inorganic carbon (DIC), and delta-C-13 profiles from seep sites on the northwestern Gulf of Mexico upper slope show anomalously negative delta-C-13 values of up to -4.5% PDB, increased levels of DIC of up to 2.45 mmole/liter, and slight alkalinity rises of up to 2.54 meq/liter, relative to water column profiles from a seep-free site (0.63%, 2.04 mmole/liter, and 2.39 meq/liter). The observed DIC enrichments coupled with the C-13-depletions are attributed to the release of CO₂ by microbial oxidation of crude oil in the seep environment, and its migration into the water column. The delta-C-13 composition of the migrating CO₂ is estimated to be -26.0% on the basis of dissolved carbon inventory. Manifestation of DIC and delta-C-13 anomalies in the water column caused by hydrocarbon seepage holds promise to be useful for hydrocarbon reconnaissance surveys over large offshore tracts on account of the simplicity of sampling acquisition, and rapidity of analytical techniques in the laboratory

Aharon, P., H. P. Schwarcz, et al. (1997). "Radiometric dating of submarine hydrocarbon seeps in the Gulf of Mexico." Geological Society of America Bulletin **109**(5): 568-579.

Massive abiogenic carbonates and calcareous shells of the chemosynthetic mytilid *Bathymodiolus* sp, containing a detailed history of hydrocarbon seepage were investigated using radiocarbon and U-series isotopes, Stable carbon isotopes and Sr-87/Sr-86 ratios were also determined in order to provide insights on the carbon source and the nature of the hydrocarbon-rich fluids, Samples from five seepage sites on the northern Gulf of Mexico sea floor overlying subsurface salt diapirs and encompassing depths from 125 to >2000 m were selected as representative of the spectrum of active and extinct seeps examined from submersible dives. In general, paired C-14 and Th-230 dates of carbonate buildups consisting of aragonite, high-Mg calcite, and dolomite mineralogies are highly discordant, The cause of the discordance, established on the basis of paired Delta(14)C and delta(13)C values (Delta(14)C = -898 parts per thousand to -992 parts per thousand; delta(13)C = -9.5 parts per thousand to -53.3 parts per thousand, for n = 27), lies with the impairment of the radiocarbon dates resulting from dilution of the C-14 pool with fossil-hydrocarbon-derived carbon. The validity of the uranium dates based on U-rich (2.4-7.6 ppm) samples is demonstrated by the concordance between U-234/U-238 and Th-230/U-234 evolution in time, and by the (U-234/U-238)(o) activity ratios that are generally

within the range of sea-water value of 1.14 ± 0.04 (2 sigma), Some dolomite-rich samples are exceptional because their (U-234/U-238)(o) ratios are significantly higher (1.22-1.38) than sea water, suggesting deposition from anoxic pore waters where the soluble U reached anomalous U-234/U-238 ratios, The formation of the carbonates from seawater-derived fluids, rather than from formation fluids advecting from deep aquifers, is supported by the Sr-87/Sr-86 composition of the samples (mean $0.709145 \pm 19 \times 10^{-6}$, $n = 14$) that compares well with modern nonseep marine carbonates and the ambient Gulf of Mexico sea water ($0.709171 \pm 8 \times 10^{-6}$), Calcareous shells, the $\delta(13)C$ values of which indicate a carbon source in sea water ($\delta(13)C = -4.3$ parts per thousand to -1.1 parts per thousand), yield valid radiocarbon ages and show fair concordancy between their radiocarbon and ionium dates, isotope migration attested by the observed U uptake in the fossil shells is likely to affect the accuracy of their ionium dates. Radiometric ages from extinct and senescent seep sites at upper bathyal depths indicate that hydrocarbon seepage occurred there during late Pleistocene time (195-13 ka), Ages derived from nascent seep sites at mid-bathyal and abyssal depths (12.3-0.0 ka) indicate that currently vigorous seepage was initiated at the end of the last deglaciation, These radiometric ages most likely reflect the time of sedimentary loading and associated salt diapirism that activated the fault conduits to the sea floor.

Aluwihare, L. I., D. J. Repeta, et al. (2002). "Chemical composition and cycling of dissolved organic matter in the Mid-Atlantic Bight." Deep-Sea Research Part II-Topical Studies in Oceanography **49**(20): 4421-4437.

This study focuses on the chemical characterization of high molecular-weight dissolved organic matter (HMW DOM) isolated from the Middle Atlantic Bight in April 1994 and March 1996. Using proton nuclear magnetic resonance spectroscopy ((¹H-NMR)-H-1) and monosaccharide analysis we compared both spatial and temporal variations in the chemical structure of HMW DOM across this region. Our analyses support the presence of at least two compositionally distinct components to HMW DOM. The major component is acyl polysaccharide (APS), a biopolymer rich in carbohydrates, acetate and lipid, accounting for between 50% and 80% of the total high molecular-weight dissolved organic carbon (HMW DOC) in surface samples. APS is most abundant in fully marine, surface-water samples, and is a product of autochthonous production. Organic matter with spectral properties characteristic of humic substances is the second major component of HMW DOM. Humic substances are most abundant (up to 49% of the total carbon) in samples collected from estuaries, near the coast, and in deep water, suggesting both marine and perhaps terrestrial sources. Radiocarbon analyses of neutral monosaccharides released by the hydrolysis of APS have similar and modern (average 71 parts per thousand) $\Delta(14)C$ values. Radiocarbon data support our suggestion that these sugars occur as part of a common macromolecule, with an origin via recent biosynthesis. Preliminary radiocarbon data for total neutral monosaccharides isolated from APS at 300 and 750m show this fraction to be substantially enriched relative to total HMW DOC and DOC. The relatively enriched radiocarbon values of APS at depth suggest

APS is rapidly transported into the deep ocean. (C) 2002 Elsevier Science Ltd.
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Amon, R. M. W. and R. Benner (1994). "RAPID-CYCLING OF HIGH-MOLECULAR-WEIGHT DISSOLVED ORGANIC-MATTER IN THE OCEAN." Nature **369**(6481): 549-552.

DISSOLVED organic matter (DOM) in the ocean is one of the largest active reservoirs of organic carbon on Earth. It is important to understand the processes by which DOM is recycled, particularly as changes in the oceanic DOM pool could affect atmospheric carbon dioxide concentrations on timescales of 1,000 to 10,000 years (ref. 1). It is commonly believed that low-molecular-weight material, which comprises 65-80% of DOM(2-5), is rapidly remineralized, and that high-molecular-weight material is refractory. But the average age of DOM in the deep ocean is about 6,000 years (ref. 6) which implies that a large proportion of the DOM cycles only very slowly. Here we present a study of the relative bioavailability of low- and high-molecular weight DOM in water samples taken from the northern Gulf of Mexico during a diatom bloom. Bacterial growth and respiration in the presence of high-molecular-weight DOM were respectively three and six times greater than for low-molecular-weight material. Although both of these pools undoubtedly contain mixtures of compounds with varying reactivities and turnover times, our results demonstrate that the bulk of oceanic DOM comprises small molecules that cycle slowly and are relatively unavailable to microorganisms.

Anderson, D. M., P. M. Glibert, et al. (2002). "Harmful algal blooms and eutrophication: Nutrient sources, composition, and consequences." Estuaries **25**(4B): 704-726.

Although algal blooms, including those considered toxic or harmful, can be natural phenomena, the nature of the global problem of harmful algal blooms (HABs) has expanded both in extent and its public perception over the last several decades. Of concern, especially for resource managers, is the potential relationship between HABs and the accelerated eutrophication of coastal waters from human activities. We address current insights into the relationships between HABs and eutrophication, focusing on sources of nutrients, known effects of nutrient loading and reduction, new understanding of pathways of nutrient acquisition among HAB species, and relationships between nutrients and toxic algae. Through specific, regional, and global examples of these various relationships, we offer both an assessment of the state of understanding, and the uncertainties that require future research efforts. The sources of nutrients potentially stimulating algal blooms include sewage, atmospheric deposition, groundwater flow, as well as agricultural and aquaculture runoff and discharge. On a global basis, strong correlations have been demonstrated between total phosphorus inputs and phytoplankton production in freshwaters, and between total nitrogen input and phytoplankton production in estuarine and marine waters. There are also numerous examples in geographic regions ranging from the largest and second largest U.S. mainland estuaries (Chesapeake Bay and the Albemarle-Pamlico Estuarine System), to the Inland Sea of Japan, the Black

Sea, and Chinese coastal waters, where increases in nutrient loading have been linked with the development of large biomass blooms, leading to anoxia and even toxic or harmful impacts on fisheries resources, ecosystems, and human health or recreation. Many of these regions have witnessed reductions in phytoplankton biomass (as chlorophyll a) or HAB incidence when nutrient controls were put in place. Shifts in species composition have often been attributed to changes in nutrient supply ratios, primarily N:P or N:Si. Recently this concept has been extended to include organic forms of nutrients, and an elevation in the ratio of dissolved organic carbon to dissolved organic nitrogen (DOC:DON) has been observed during several recent blooms. The physiological strategies by which different groups of species acquire their nutrients have become better understood, and alternate modes of nutrition such as heterotrophy and mixotrophy are now recognized as common among HAB species. Despite our increased understanding of the pathways by which nutrients are delivered to ecosystems and the pathways by which they are assimilated differentially by different groups of species, the relationships between nutrient delivery and the development of blooms and their potential toxicity or harmfulness remain poorly understood. Many factors such as algal species presence/abundance, degree of flushing or water exchange, weather conditions, and presence and abundance of grazers contribute to the success of a given species at a given point in time. Similar nutrient loads do not have the same impact in different environments or in the same environment at different points in time. Eutrophication is one of several mechanisms by which harmful algae appear to be increasing in extent and duration in many locations. Although important, it is not the only explanation for blooms or toxic outbreaks. Nutrient enrichment has been strongly linked to stimulation of some harmful species, but for others it has not been an apparent contributing factor. The overall effect of nutrient over-enrichment on harmful algal species is clearly species specific.

Argyrou, M. E., T. S. Bianchi, et al. (1997). "Transport and fate of dissolved organic carbon in the Lake Pontchartrain estuary, Louisiana, USA." Biogeochemistry **38**(2): 207-226.

Cycling dynamics of dissolved organic carbon (DOC) were examined in Lake Pontchartrain estuary, Louisiana, in relation to changes in freshwater inputs. DOC concentrations ranged from 5.3 to 8.5 mg C L⁻¹ reaching their highest during high river inflow. The percentage of DOC represented by HMW DOC (or colloidal material) was greatest (ca. 11%) at stations where freshwater discharge from rivers and surrounding wetlands was most significant. Moreover, the lignin-phenol content of this material (λ ranged from 0.09 to 0.33 and Λ from 0.11 to 0.39) confirmed that a significant fraction of colloidal organic carbon was derived from terrestrial sources. Riverine and benthic fluxes represented the dominant sources of DOC to the estuary. On an annual basis, riverine and benthic DOC concentrations were estimated to be 2.8×10^{10} g C yr⁻¹ and 8.8×10^{10} g C yr⁻¹, respectively, while the total DOC pool in the estuary was 3.8×10^{10} g C. Annual average concentrations of dissolved inorganic carbon (DIC) (1298 μ M) and pCO₂ (5774 μ atm) were

comparable to those found in other freshwater systems that reached CO₂ saturation levels. Net losses of DOC in the Lake Pontchartrain estuary appeared to be primarily controlled by heterotrophic consumption (conversion of CO₂)- which may have been amplified by the long residence time (approximately 120 days) of DOC in this system.

Arvidson, R. S., J. W. Morse, et al. (2004). "The sulfur biogeochemistry of chemosynthetic cold seep communities, Gulf of Mexico, USA." Marine Chemistry **87**(3-4): 97-119.

In hydrocarbon seep sediments associated with chemosynthetic communities along the continental slope of the northern Gulf of Mexico, the distribution of sulfate reduction rates is very heterogeneous, with rates ranging from values typical of off-seep Gulf environments to very high rates (up to similar to 14.8 $\mu\text{mol cm}^{-3} \text{ day}^{-1}$). These extreme rates deplete porewater sulfate within 20 cm and are associated with increases in dissolved sulfide and DIC concentrations. Large depletions of porewater calcium and high concentrations of solid phase CaCO₃ indicate that carbonate precipitation is driven by sulfate reduction as well. Although total organic carbon concentrations (reflecting an unresolved mix of ambient biomass, crude oil and other seep hydrocarbons) are much higher than elsewhere in the Gulf, sulfate reduction rates are not related in any simple fashion to POC. In addition, apparent diffusion coefficients (D-S*) computed from sulfate gradients and reduction rates typically exceed molecular values. In tubeworm-Beggiatoa mat associations these excursions approach two orders of magnitude. We suggest that these elevated D-S* values may indicate specific organism-sediment interactions that replenish sulfate, either through sediment irrigation or in situ sulfur recycling. Interactions between Beggiatoa and tubeworms may lead to large enhancements of the apparent flux of sulfate to the zone of SR, and give rise to very high SR rates that are otherwise probably limited in duration and lateral extent. (C) 2004 Elsevier B.V. All rights reserved.

Baskaran, M., P. H. Santschi, et al. (1992). "SCAVENGING OF THORIUM ISOTOPES BY COLLOIDS IN SEAWATER OF THE GULF OF MEXICO." Geochimica Et Cosmochimica Acta **56**(9): 3375-3388.

A suite of surface-water samples from the Gulf of Mexico was analyzed to ascertain the extent of association of Th isotopes (Th-232, Th-234) with colloids and the role of colloidal material in scavenging Th from the water column. These are the first measurements of naturally occurring colloidal Th. The fraction of Th-232, Th-234 associated with colloids (i.e., 10,000 Dalton < colloids < 0.4 μm) ranged from 10 to 78% of the Th passing 0.4 μm Nucleopore cartridge filters. Colloid mass concentrations were much larger than the corresponding 0.4 μm filter-retained particle concentrations. The conditional partitioning constants for Th-234 with colloids, K(c), and filter-retained particles, K(f), are comparable in magnitude. Thorium scavenging rate constants decreased in value with increasing distance from the coast (0.164 to 0.007 d⁻¹), and this is attributed to the decreasing particulate-matter concentration from coastal to deeper Gulf waters. In addition, there exists a highly significant, positive correlation between

values of the Th scavenging rate constant and the fraction of 0.4 μm filter-passing Th associated with colloids. An average residence time of 6 days, with a range of 4-26 days, was calculated for the characteristic time scale of colloid transfer through the particle size spectrum, including sedimentation. The large fraction of Th-234 which was found to be associated with colloids suggests that Th isotopes can be used as in-situ "coagulometers," tracing the aggregation of colloidal material with, or into, large aggregates of filter-retained sizes.

Baskaran, M., P. H. Santschi, et al. (1996). "Th-234:U-238 disequilibria in the Gulf of Mexico: The importance of organic matter and particle concentration." Continental Shelf Research **16**(3): 353-380.

We have measured the concentrations of dissolved and particulate Th-234, suspended particulate matter, dissolved organic carbon, nutrients and a suite of pigments along a transect in the shelf and slope waters of the Gulf of Mexico. The deep water station samples were collected in the presence (summer 1992) and absence (spring 1992) of a warm-core ring. In the summer: the station was at the periphery of a warm-core ring containing more oligotrophic, Caribbean water, while in the spring, only Gulf water was present. The Th-234 deficiency, which extends throughout a 1500 m water column in spring, indicates active lateral exchange of dissolved and particulate species. This study provides insight into the role of particles for Th-234 scavenging and differences in the scavenging intensities in the presence and absence of a warm-core ring. In addition, the possibility that the major carrier phase of thorium cycling could be dissolved organic carbon is suggested from the correlation between Th-234 (dissolved and total) and dissolved organic carbon concentrations. The average particle residence time for the whole water column in spring, seven days, was significantly shorter than that for summer, 21 days. This longer residence time in the summer is attributed to the presence of a warm-core ring which resulted in lower particle, DOC, and nutrient concentrations. Values of scavenging and particle residence times and Th-234 fluxes, and the significance of the correlations of these values with concentrations of particle mass and various pigments are discussed.

Beauchamp, B. (2004). "Natural gas hydrates: myths, facts and issues." Comptes Rendus Geoscience **336**(9): 751-765.

Gas hydrates are solid-like substances naturally occurring beneath the oceans and in polar regions. They contain vast, and potentially unstable, reserves of methane and other natural gases. Many believe that, if released in the environment, the methane from hydrates would be a considerable hazard to marine ecosystems, coastal populations and infrastructures, or worse, that it would dangerously contribute to global warming. On the other hand, hydrates may contain enough natural gas to provide an energy supply assurance for the 21st century. This paper attempts to separate the myths, the facts and the issues that relate to natural gas hydrates beyond the doomsday environmental scenarios and overly optimistic estimates. (C) 2004 Academie des sciences. Published by Elsevier SAS. All rights reserved.

Benner, R. and B. Biddanda (1998). "Photochemical transformations of surface and deep marine dissolved organic matter: Effects on bacterial growth." Limnology and Oceanography **43**(6): 1373-1378.

The effects of photochemical transformations on the bioavailability of marine dissolved organic matter (DOM) were investigated in surface and deep water from the Gulf of Mexico. Seawater samples were collected from eight depths (15-1,000 m), passed through 0.2- μ m pore-size filters, and exposed to sunlight in quartz bottles in a flowing seawater deck incubator for 5-9 h. Following sunlight exposure, samples were inoculated (1:10) with unfiltered seawater from 15-m depth, and bacterial growth rates were estimated from rates of H-3-leucine incorporation in dark incubations. Exposure of surface-water DOM to sunlight resulted in a 75% reduction in bacterial production, whereas exposure of deep-water DOM resulted in a 40% enhancement in bacterial production. Photomineralization of bioreactive DOM likely contributed to the reduction of bacterial growth in surface water, but the photoproduction of biorefractory DOM also appeared to contribute to reduced bacterial growth. Enhanced bacterial growth in irradiated deep water was consistent with previous studies demonstrating the photoproduction of bioavailable substrates from deep-water DOM. Phototransformations of DOM appeared to be multifaceted and to play a critical role in the cycling of DOM in the ocean.

Benner, R. and S. Opsahl (2001). "Molecular indicators of the sources and transformations of dissolved organic matter in the Mississippi river plume." Organic Geochemistry **32**(4): 597-611.

The dynamics of dissolved organic matter (DOM) in the Mississippi river plume were investigated during four cruises to the region in 1990-1993. During each cruise, large-volume water samples were collected from a broad salinity gradient (0-36 psu) for the determination of dissolved organic carbon (DOC) concentrations and the isolation of DOM by tangential-flow ultrafiltration. The fraction of DOC recovered by ultrafiltration ranged from 49% in the river to 22% in the Gulf of Mexico. The ultrafiltered DOM (UDOM) was further characterized for the concentrations and compositions of combined neutral sugars and lignin-derived phenols. Concentrations of DOC ranged from 359 μ M in the river during the summer to 65 μ M in surface waters of the Gulf of Mexico during the winter. Mixing curves indicated minor losses of DOC at low salinities and a major source of DOC at mid salinities. Combined neutral sugars had elevated concentrations at mid salinities where plankton biomass and rates of autotrophic and heterotrophic processes were maximal, indicating that elevated concentrations of sugars and DOC were freshly-derived from plankton. In contrast, concentrations of lignin phenols in UDOM were depicted at low salinities, indicating losses due to flocculation of terrestrially-derived humic substances. The selective removal of syringyl phenols from dissolved lignin was observed in UDOM from higher salinity (> 25 psu) waters, providing the first molecular evidence of the removal of terrigenous DOM from the coastal ocean due to photooxidation. Together, these molecular biomarkers indicated much

greater dynamic behavior of DOM than was apparent from bulk DOC analyses, and they demonstrated that biological as well as physico-chemical processes were important in controlling the concentrations and compositions of DOM in coastal waters. (C) 2001 Elsevier Science Ltd. All rights reserved.

Bernot, M. J. and W. K. Dodds (2005). "Nitrogen retention, removal, and saturation in lotic ecosystems." Ecosystems **8**(4): 442-453.

Increased nitrogen (N) loading to lotic ecosystems may cause fundamental changes in the ability of streams and rivers to retain or remove N due to the potential for N saturation. Lotic ecosystems will saturate with sustained increases in the N load, but it is unclear at what point saturation will occur. Rates of N transformation in lotic ecosystems will vary depending on the total N load and whether it is an acute or chronic N load. Nitrogen saturation may not occur with only pulsed or short-term increases in N. Overall, saturation of microbial uptake will occur prior to saturation of denitrification of N and denitrification will become saturated prior to nitrification, exacerbating increases in nitrate concentrations and in N export downstream. The rate of N export to downstream ecosystems will increase proportionally to the N load once saturation occurs. Long term data sets showed that smaller lotic ecosystems have a greater capacity to remove in-stream N loads, relative to larger systems. Thus, denitrification is likely to become less important as a N loss mechanism as the stream size increases. There is a great need for long-term studies of N additions in lotic ecosystems and clear distinctions need to be made between ecosystem responses to short-term or periodic increases in N loading and alterations in ecosystem functions due to chronic N loading.

Bianchi, T. S., M. Baskaran, et al. (1997). "Carbon cycling in a shallow turbid estuary of Southeast Texas: The use of plant pigment biomarkers and water quality parameters." Estuaries **20**(2): 404-415.

Particulate organic carbon (POC), dissolved organic carbon (DOC), and plant pigments (chlorophylls and carotenoids) were measured approximately bimonthly from March 1992 to October 1993 in the Sabine-Neches estuary (Sabine Lake region), located on the Texas-Louisiana border. High freshwater inflow into this shallow turbid estuary results in the shortest hydraulic residence time (ca. 7 d) of all Texas estuaries (Baskaran et al. in press). Annual averages of chlorophyll-a ($3.0 \mu\text{g l}^{-1}$) and particulate organic carbon (1.1 mg l^{-1}) in the water column were extremely low in comparison to other shallow estuaries. The highest chlorophyll-a concentrations were observed in October 1993, in the mid and lower regions of the estuary, during the lowest river discharge. Zeaxanthin and fucoxanthin concentrations suggested that much of the chlorophyll-a during this low flow period was represented by cyanobacteria and diatoms that entered from the Gulf of Mexico. The range of DOC concentrations was generally high ($4.4\text{-}20.9 \text{ mg l}^{-1}$) and were significantly correlated with POC, but not with chlorophyll-a concentrations. When total suspended particulate (TSP) concentrations were below 20 to 30 mg l^{-1} , there were significant increases in %POC and %PON of the TSP. The unusually high POC: chlorophyll-a ratios

(highest value of 1423) suggested that much of the POC contained low concentrations of chlorophyll-a that had degraded during transport from wetlands in the Sabine and Neches rivers. Based on these data, this estuary can be characterized as a predominantly heterotrophic system, with low light penetrance, short particle-residence times, high DOC, and low inputs from autochthonous carbon sources.

Bianchi, T. S., T. Filley, et al. (2004). "Temporal variability in sources of dissolved organic carbon in the lower Mississippi River." Geochimica Et Cosmochimica Acta **68**(5): 959-967.

Here we report on the temporal changes in the composition of dissolved organic carbon (DOC) collected in the tidal freshwater region of the lower Mississippi River. Lignin-phenols, bulk stable carbon isotopes, compound-specific isotope analyses (CSIA) and C-13 nuclear magnetic resonance (NMR) spectrometry were used to examine the composition of high molecular weight dissolved organic matter (HMW DOM) at one station in the lower river over 6 different flow regimes in 1998 and 1999. It was estimated that the annual input of DOC delivered to the Gulf of Mexico from the Mississippi River was of 3.1×10^{-3} Pg, which represents 1.2% of the total global input of DOC from rivers to the ocean. Average DOC and HMW DOC were 489 ± 163 and 115 ± 47 μ M, respectively. C-13-NMR spectra revealed considerably more aliphatic structures than aromatic carbons in HMW DOC. Lignin phenols were significantly C-13-depleted with respect to bulk HMW DOM indicating that C-4 grass inputs to the HMW DOM were not significant. It is speculated that C-4 organic matter in the river is not being converted (via microbial decay) to HMW DOM as readily as C-3 organic matter is, because of the association of C-4 organic matter with finer sediments. The predominantly aliphatic C-13 NMR signature of HMW DOM suggests that autochthonous production in the river may be more important as a source of DOC than previously thought. Increases in nutrient loading and decreases in the suspended load (because of dams) in the Mississippi River, as well as other large rivers around the world, has resulted in significant changes in the sources and overall cycling of riverine DOC. Copyright (C) 2004 Elsevier Ltd.

Bianchi, T. S., J. J. Galler, et al. (2007). "Hydrodynamic sorting and transport of terrestrially derived organic carbon in sediments of the Mississippi and Atchafalaya Rivers." Estuarine Coastal and Shelf Science **73**(1-2): 211-222.

Over the course of two years, four cruises were conducted at varying levels of discharge in the lower Mississippi and Atchafalaya Rivers (MR and AR) where grab samples were collected from sand- and mud-dominated sediments. The tetramethylammonium hydroxide (TMAH) thermochemolysis method was used to determine sources of terrestrially derived organic carbon (OC) in these two sediment types, to examine the effects of hydrodynamic sorting on lignin sources in river sediments. Average lignin concentrations in the lower MR were 1.4 ± 1.1 mg gOC(-1) at English Turn (ET) and 10.4 ± 27.4 mg gOC(-1) at Venice. Using these concentrations, annual lignin fluxes to the Gulf of Mexico, from tidal and estuarine mud remobilization at ET and Venice, were $3.1 \pm 2.5 \times 10^5$ kg and

11.4 +/- 30.0 x 10⁵ kg, respectively. Much of the lignin-derived materials in muddy sediments appeared to be derived from non-woody grass-like sources - which should decay more quickly than the woody materials typically found in the sandy deposits. The average total OC% (1.93 +/- 0.47) of English Turn sands yields an annual flux of 0.34 +/- 0.09 x 10⁹ kg. Lignin flux in the English Turn sands (3.6 +/- 2.6 mg gC⁻¹) using the numbers above would be 12.2 +/- 9.4 x 10⁵ kg. The extensive amounts of sand-sized woody materials (coffee-grinds) found in the sandy sediments in both the AR and MR are likely derived from woody plant materials. This is the first time it has been demonstrated that sandy sediments in the MR provide an equally important pathway (compared to muds) for the transport of terrestrially derived organic matter to the northern Gulf of Mexico. Using the AR average %OC in sand (116 +/- 0.72), we estimated an annual flux of OC to the shelf of 0.13 +/- 10.0(7) x 10⁹ kg. Lignin flux for AR sands was estimated to be 12.4 +/- 12.1 x 10⁵ kg. Despite the high error associated with these numbers, we observe for the first time that the flux of lignin in sandy sediments in the AR to the northern Gulf of Mexico is comparable to that found in the MR. These results further support the likelihood of grain-size related hydrodynamic sorting of terrestrially derived organic carbon in the lower Mississippi and Atchafalaya Rivers, suggesting that there is a distinct sandy sediment organic fraction contributed by major rivers to the global carbon cycle. (C) 2007 Elsevier Ltd. All rights reserved.

Bianchi, T. S., C. Lambert, et al. (1994). "PLANT PIGMENTS AS BIOMARKERS OF COLLOIDAL ORGANIC-CARBON IN THE GULF-OF-MEXICO." Abstracts of Papers of the American Chemical Society **207**: 92-GEOC.

Bianchi, T. S., C. Lambert, et al. (1995). "PLANT PIGMENTS AS BIOMARKERS OF HIGH-MOLECULAR-WEIGHT DISSOLVED ORGANIC-CARBON." Limnology and Oceanography **40**(2): 422-428.

We used plant pigments as tracers of high-molecular-weight dissolved organic C (HMW DOG) (<0.2 μm and >1,000 Da). Water samples were collected from four stations along a transect on cruises in June 1992 and January 1993 in the Gulf of Mexico. Samples were also collected from three stations on the continental shelf of Cape Hatteras for comparison. Chlorophylls a and b were at detectable levels in HMW DOG; concentrations of the carotenoids zeaxanthin and fucoxanthin in HMW DOC indicated that cyanobacteria, prochlorophytes, and diatoms contributed to the total HMW DOC pool across the continental margin in the gulf. The extremely low concentrations of pheopigments (except for chlorophyllide) in particulate organic C and HMW DOC suggested that direct exudation from phytoplankton and sloppy feeding by zooplankton were the major mechanisms of release. However, significant and selective pigment loss, due to light and thermal degradation in the reservoir, did occur in the absence of any cooling or light-shielding precautions. This study demonstrated that pigments can be used to acquire qualitative information on the sources of HMW DOC and to gain insight on its relative age-based on pigment turnover.

Bianchi, T. S., C. D. Lambert, et al. (1997). "Sources and transport of land-derived particulate and dissolved organic matter in the Gulf of Mexico (Texas shelf/slope): The use of lignin-phenols and loliolides as biomarkers." Organic Geochemistry **27**(1-2): 65-78.

The fate and transport of terrestrial organic matter across the continental margin in the Gulf of Mexico was studied in 1992 and 1993 using chemical biomarkers. Lignin-phenols were utilized as biomarkers for terrestrial inputs and indicated that much of the terrestrial organic matter inputs were deposited on the shelf/break and slope. The lignin-phenol concentrations (normalized to carbon) in POC, HMW DOC, and sediments in slope waters were considerably higher than at other open ocean sites studied previously. The dominant mechanism for transport of terrestrially-derived POC and HMW DOC across the shelf and slope was hypothesized to be advection of riverine and estuarine discharges through benthic nepheloid layers. Based on loliolide concentrations in the water column, we believe that lateral transport of these materials at the shelf/break (through extensions of benthic nepheloid layers) may have been an important mechanism for the injection of terrestrially-derived organic matter into deep slope waters. (C) 1997 Elsevier Science Ltd.

Bianchi, T. S., S. Mitra, et al. (2002). "Sources of terrestrially-derived organic carbon in lower Mississippi River and Louisiana shelf sediments: implications for differential sedimentation and transport at the coastal margin." Marine Chemistry **77**(2-3): 211-223.

In this study, we examined the temporal and spatial variability of terrestrial organic carbon sources in lower Mississippi River and Louisiana shelf sediments (during 11 cruises over a 22-month period) to further understand the sorting dynamics and selective transport of vascular plant materials within the primary dispersal system of the river. Bulk $\delta^{13}\text{C}$ values in lower river sediments ranged from -21.90 parts per thousand to -24.64 parts per thousand (mean = -23.20 \pm 1.09 parts per thousand), these values were generally more depleted than those found in shelf sediments (-22.5 parts per thousand to -21.2 parts per thousand). The $\Lambda(8)$ ($\Lambda(8)$ = sum of vanillyl, syringyl and cinnamyl phenols produced from the oxidation of 100 mg of organic carbon) values in the lower river ranged from 0.71 to 3.74 (mean = 1.78 \pm 0.23). While there was no significant relationship between $\Lambda(8)$ and river discharge ($p > 0.05$), the highest value occurred during peak discharge in April 1999 which corresponded to the highest observed C/N value of 17.41. The $\Lambda(8)$ values on the shelf ranged from 0.68 to 1.36 (mean = 0.54 \pm 0.30) and were significantly lower ($p < 0.05$) than the average value for lower river sediments. The range of S/V (syringyl/vanillyl) and C/V (cinnamyl/vanillyl) ratios on the shelf, 0.11 to 0.95 and 0.01 to 0.08, respectively, were similar to that found in the lower river. These low C/V ratios are indicative a mixture of woody and non-woody carbon sources. Recent work by Goni et al. [Nature 389 (1997) 275; Geochim. Cosmochim. Acta 62 (1998) 3055], which, did not include sampling transects within the primary dispersal system of the Mississippi River, showed a non-woody vascular plant signature on the Louisiana shelf. This suggests that riverine-derived, woody tissues preferentially settle out of the water column, in the lower river and inner

shelf, prior to the selective dispersal of C-3 versus C-4 non woody materials in other regions the shelf and slope. This work further demonstrates the importance of differential settlement of particles, sampling location within the dispersal system, and river discharge, when examining biogeochemical cycles in river-dominated margins. (C) 2002 Elsevier Science B.V. All rights reserved.

Bianchi, T. S., L. A. Wysocki, et al. (2007). "Temporal variability in terrestrially-derived sources of particulate organic carbon in the lower Mississippi River and its upper tributaries." Geochimica Et Cosmochimica Acta **71**(18): 4425-4437.

In this study, we examined the temporal changes of terrestrially-derived particulate organic carbon (POC) in the lower Mississippi River (MR) and in a very limited account, the upper tributaries (Upper MR, Ohio River, and Missouri River). We used for the first time a combination of lignin-phenols, bulk stable carbon isotopes, and compound-specific isotope analyses (CSIA) to examine POC in the lower MR and upper tributaries. A lack of correlation between POC and lignin phenol abundances ($\delta^{13}C$) was likely due to dilution effects from autochthonous production in the river, which has been shown to be considerably higher than previously expected. The range of $\delta^{13}C$ values for p-hydroxycinnamic and ferulic acids in POC in the lower river do support that POM in the lower river does have a significant component of C-4 in addition to C-3 source materials. A strong correlation between $\delta^{13}C$ values of p-hydroxycinnamic, ferulic, and vanillyl phenols suggests a consistent input of C3 and C4 carbon to POC lignin while a lack of correlation between these same phenols and POC bulk $\delta^{13}C$ further indicates the considerable role of autochthonous carbon in the lower MR POC budget. Our estimates indicate an annual flux of POC of 9.3×10^8 kg y^{-1} to the Gulf of Mexico. Total lignin fluxes, based on As values of POC, were estimated to be 1.2×10^5 kg y^{-1} . If we include the total dissolved organic carbon (DOC) flux (3.1×10^9 kg y^{-1}) reported by [Bianchi T. S., Filley T., Dria K. and Hatcher, P. (2004) Temporal variability in sources of dissolved organic carbon in the lower Mississippi River. *Geochim. Cosmochim. Acta* 68, 959-967.], we get a total organic carbon flux of 4.0×10^9 kg y^{-1} . This represents 0.82% of the annual total organic carbon supplied to the oceans by rivers (4.9×10^{11} kg). (C) 2007 Elsevier Ltd. All rights reserved.

Biddanda, B. and R. Benner (1997). "Major contribution from mesopelagic plankton to heterotrophic metabolism in the upper ocean." Deep-Sea Research Part I-Oceanographic Research Papers **44**(12): 2069-2085.

Measurement of plankton respiration and heterotrophic bacterial abundance and production were made at seven deep water stations within the upper 500 m of the Gulf of Mexico during the summer of 1995. Bacterial abundance [$(1.1-4.6) \times 10^8$ l^{-1}] and rates of bacterial production (2-19 nM C h^{-1}) and plankton respiration (50-245 nM O_2 h^{-1}) decreased with depth by four-to nine-fold, and were similar to those reported for oligotrophic waters. Bacterial turnover times increased with depth from approximately 1 to 5 days. Bacterial growth efficiencies decreased from 15% at the surface to 8% at 500 m.

Depth-integrated plankton respiration exceeded known estimates of primary production for the region, suggesting that heterotrophic utilization of previously and concurrently produced organic matter (e.g. spring phytoplankton growth, and summer blooms of *Trichodesmium* sp.) was occurring during the summer. Estimates for the upper 500 m showed that roughly half of the bacterial biomass (56%), bacterial production (49%), and plankton respiration (60%) occurred below the euphotic zone. Routine oceanographic studies have focused exclusively on the metabolic activity occurring within the euphotic zone. Our measurements, however, indicate that mesopelagic plankton also contribute substantially to heterotrophic metabolism and nutrient cycling in the ocean. (C) 1998 Elsevier Science Ltd.

Biddanda, B., S. Opsahl, et al. (1994). "PLANKTON RESPIRATION AND CARBON FLUX THROUGH BACTERIOPLANKTON ON THE LOUISIANA SHELF." Limnology and Oceanography **39**(6): 1259-1275.

Carbon flow through bacterioplankton can be evaluated only if both growth and respiration are known. Measurements of community and bacterial respiration (oxygen consumption) and bacterial production ($[H-3]$ leucine incorporation) were made in highly productive shelf and less productive slope waters in the northern Gulf of Mexico. Rates of bacterial production and community respiration, as well as bacterial abundance and dissolved organic C concentrations, declined with depth at both locations. Water-column bacterial production ranged from 0.1 to 3.1 $\mu\text{g C liter}^{-1} \text{ h}^{-1}$, and community respiration rates ranged from 0.05 to 0.45 $\mu\text{M O}_2 \text{ h}^{-1}$. In comparison to the slope, the shelf was characterized by 2-fold higher bacterial abundance and bacterial production but similar community respiration rates. Estimated production per bacterium values decreased logarithmically with depth (1.4-0.15 $\text{fg C cell}^{-1} \text{ h}^{-1}$) and were similar at both locations. Estimated respiration per bacterium values for the surface water ranged from 0.10 to 0.36 $\text{fmol O}_2 \text{ cell}^{-1} \text{ h}^{-1}$ and were higher on the slope than the more densely populated shelf. A selective suppression of bacterial respiration occurred under both natural and experimentally (tangential-flow ultrafiltration) enhanced bacterial abundances. Measured growth efficiencies fell between 26 and 55%, with higher efficiencies occurring on the shelf (50%) than the slope (26%). Bacterioplankton at the less productive slope station processed a larger daily share of local primary production (69%) than bacteria at the highly productive shelf station (25%).

Bierbaum, R. (2002). "The role of science in federal policy development on a regional to global scale: Personal commentary." Estuaries **25**(4B): 878-885.

Nutrient enrichment of coastal waters is an example of the large-scale, highly complex environmental challenges facing decision makers today. Conventional monitoring networks and advanced observational capabilities permit the detection of changes in the environment at continental to global scales (e.g., hypoxia in the Gulf of Mexico, aerosol plumes stretching across the ocean, global atmospheric enrichment of carbon dioxide). Much more knowledge is needed, however, to fully understand the societal consequences of environmental change

and of actions taken to address them. This paper discusses the emerging role of assessment in developing effective U.S. policy responses to large-scale, complex environmental change while improving the scientific understanding of the problem. In the cases of global climate change and coastal hypoxia, the U.S. Congress passed legislation authorizing assessments recognizing that decision making must proceed in the face of scientific uncertainty. Evaluating the state of knowledge is usually the first step in an assessment in order to provide a picture of what is known and where there are knowledge gaps. Assessments should also provide the policy maker with an idea of the level of uncertainty, how long it may take to reduce the uncertainty, what information is most critical to resolve, and the consequences and benefits of the various management options. In this paper I draw upon several examples from national assessments, including those of climate change impacts on the U.S. and relationships between Mississippi River water and Gulf of Mexico water quality, to illustrate the strengths and difficulties of using science and assessment to inform the policy process.

Bissett, W. P., R. Arnone, et al. (2005). "Predicting the optical properties of the West Florida Shelf: resolving the potential impacts of a terrestrial boundary condition on the distribution of colored dissolved and particulate matter." Marine Chemistry **95**(3-4): 199-233.

Predicting the distribution of Inherent Optical Properties (IOPs) in the water column requires predicting the physical, chemical, biological, and optical interactions in a common framework that facilitates feedback responses. This work focuses on the development of ecological and optical interaction equations embedded in a 2D hindcast model of the shallow water optical properties on the West Florida Shelf (WFS) during late summer/fall of 1998. This 2D simulation of the WFS includes one case with a Loop Current intrusion above the 40-m isobath and one with the Loop Current intrusion in addition to a periodic terrestrial nutrient supply below the 10-m isobath. The ecological and optical interaction equations are an expansion of a previously developed model for open ocean conditions (Bissett, W.P., Carder, K.L., Walsh, J.J., Dieterle, D.A., 1999a. Carbon cycling in the upper waters of the Sargasso Sea: II. Numerical simulation of apparent and inherent optical properties. *Deep-Sea Research, Part 1: Oceanographic Research Papers*, 46 (2), 271-317; Bissett, W.P., Walsh, J.J., Dieterle, D.A., Carder, K.L., 1999b. Carbon cycling in the upperwaters of the Sargasso Sea: I. Numerical simulation of differential carbon and nitrogen fluxes. *Deep-Sea Research, Part 1: Oceanographic Research Papers*, 46 (2), 205-269). The expansion includes an increase in the number of elemental pools to include silica, phosphorus, and iron, an increase in the number of phytoplankton functional groups, and a redevelopment of the Dissolved Organic Matter (DOM) and Colored Dissolved Organic Matter (CDOM) interaction equations. It was determined from this simulation that while the Loop Current alone was able to predict the water column conditions present during the summer, the Loop Current alone was not enough to simulate the magnitude of optical constituents present in the fall of 1998 when compared to satellite imagery. Simulating terrestrial inorganic and organic nutrients and CDOM pulses coinciding with significant

meteorological events and high freshwater pulses released from the major rivers feeding the WFS were required to accurately predict the distribution and scale of the inherent optical properties at the surface during the fall months. Modeling the in situ light field for phytoplankton growth and community competition requires addressing the CDOM optical constituent explicitly. The majority of the annually modeled CDOM on WFS was created via in situ production; however, it was also rapidly removed via advection and photochemical destruction. A pulse of terrestrial nutrient and organic color was required to simulate the dramatic changes in surface color seen in satellite imagery on the WFS. The dynamics of the biogeochemical portion of the simulation demonstrate the importance of nonstoichiometric supplies of terrestrial nutrients on the WFS to the prediction of nutrient and CDOM fluxes. (C) 2004 Elsevier B.V. All rights reserved.

Bissett, W. P., J. J. Walsh, et al. (1999). "Carbon cycling in the upper waters of the Sargasso Sea: I. Numerical simulation of differential carbon and nitrogen fluxes." Deep-Sea Research Part I-Oceanographic Research Papers **46**(2): 205-269.

A complex ecosystem model is developed for the area around Bermuda in the Sargasso Sea. The model is physically driven by seasonal changes in spectral light, temperature, and water column mixing. Autotrophic growth is represented by four functional groups of phytoplankton. The groups have light and nutrient utilization characteristics that reflect those of *Prochlorococcus*, *Synechococcus* and *Chromophycota* species. The model includes differential carbon and nitrogen cycling, nitrification, and nitrogen fixation to effect realistic allochthonous and autochthonous nutrient sources to the euphotic zone. This simulation yields realistic seasonal and vertical (1) succession of phytoplankton functional groups' biomass, productivity, and pigments; (2) profiles of dissolved inorganic carbon, nitrate, and ammonium; and (3) fluxes of carbon dioxide at the air-sea boundary and particulate carbon and nitrogen settling losses, when compared to the JGOFS BATS site. The addition of local nitrification, differential carbon and nitrogen remineralization, and nitrogen fixation removes the need for an unrealistically high upward vertical flux of nitrate to mimic the productivity and chlorophyll a stocks. The explicit numerical description of carbon and nitrogen utilization by heterotrophic bacteria simulated a population that was not nitrogen-limited in these waters. Instead, the heterotrophic bacteria community was limited by energy resources in the form of DOC, and was a nitrogen source for the autotrophic community through the excretion of excess NH_4 from the labile DOM energy source. Numerical descriptions of ecosystems based solely on nitrogen dynamics, or fixed carbon to nitrogen ratios, may yield an inaccurate prediction of carbon and nitrogen fluxes, and fail to properly predict the carbon cycle. © 1998 Elsevier Science Ltd. All rights reserved.

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Bondavalli, C., R. E. Ulanowicz, et al. (2000). "Insights into the processing of carbon in the South Florida Cypress Wetlands: a whole-ecosystem approach using network analysis." Journal of Biogeography **27**(3): 697-710.

Aim The aim of this research was to investigate the potential of the South Florida Cypress Wetlands as a carbon-accumulating system. **Location** This ecosystem is part of the Big Cypress Natural Preserve, located in the south-west part of Florida (USA) between the Mangrove Swamps that border the Gulf of Mexico and the Everglades. **Methods** This investigation was carried out by constructing networks of carbon exchange between the living and nonliving components that comprise this ecosystem. By means of these networks potential for carbon accumulation has been assessed by identifying and quantifying pathways for the transfer of carbon, assessing the efficiency between trophic levels, and evaluating the importance of material cycling. These analyses are commonly referred to as network analysis. **Results** Results obtained show that dependency on detritus by higher trophic levels is rather low and so is the trophic efficiency. Yet, less than 10% of the carbon that flows through the system is recycled and the magnitude of internal ascendancy reaches only 40% of the total system ascendancy. **Main conclusions** All these results support the hypothesis that the South Florida Cypress Wetlands are predominately flow-through in nature and that carbon accumulation in this environment is noticeable.

Boody, G., B. Vondracek, et al. (2005). "Multifunctional agriculture in the United States." Bioscience **55**(1): 27-38.

We evaluated possible changes to current farming practices in two Minnesota watersheds to provide insight into how farm policy might affect environmental, social, and economic outcomes. Watershed residents helped develop four scenarios to evaluate alternative future trends in agricultural management and to

project potential economic and environmental outcomes. We found that environmental and economic benefits can be attained through changes in agricultural land management without increasing public costs. The magnitude of these benefits depends on the magnitude of changes to agricultural practices. Environmental benefits include improved water quality, healthier fish, increased carbon sequestration, and decreased greenhouse gas emissions, while economic benefits include social capital formation, greater farm profitability; and avoided costs. Policy transitions that emphasize functions of agriculture in addition to food production are crucial for creating change We suggest that redirecting farm payments by using alternative incentives could lead to substantial environmental changes at little or no extra cost to the taxpayer.

Botello, A. V., E. F. Mandelli, et al. (1980). "ORGANIC-CARBON ISOTOPE RATIOS OF RECENT SEDIMENTS FROM COASTAL LAGOONS OF THE GULF-OF-MEXICO, MEXICO." Geochimica Et Cosmochimica Acta **44**(3): 557-559.

Breed, G. A., G. A. Jackson, et al. (2004). "Sedimentation, carbon export and food web structure in the Mississippi River plume described by inverse analysis." Marine Ecology-Progress Series **278**: 35-51.

The Mississippi River stimulates the coastal marine ecosystem directly with dissolved organic matter and indirectly with inorganic nutrients that enhance primary production. To understand the river's effect, we need to track the fate of both sources of organic matter. Using readily available data, we investigated the planktonic ecosystem of the buoyant Mississippi River plume using an inverse analysis technique to describe the carbon flow for the complete planktonic system. For each season we divided the marine waters receiving Mississippi River discharge into 4 dilution regions connected by movement of river water. Our results show that during 3 seasons (spring, summer, and fall) mid-salinity waters (15 to 29 psu) exported organic matter (strongly net autotrophic), whereas the other regions imported it (net heterotrophic). More than 20% of total plume primary productivity was exported from the entire modeled region, as continued water movement carried organic carbon into surrounding waters. In contrast, the winter plume was net-heterotrophic everywhere, as high bacterial respiration overwhelmed relatively low primary production, and riverine dissolved organic carbon (DOC) and organic carbon from resuspended sediments were required to balance a carbon deficit. From the spring through fall, sedimentation of organic carbon was linked to primary production, with strongest sedimentation in mid-salinity regions. Sedimentation was enhanced beneath less productive, higher-salinity regions, by import of organic carbon moving out of mid-salinity regions. In contrast, winter organic carbon sedimentation rates were calculated to be zero in all model regions. The analysis showed a dynamic relationship between primary production and sedimentation and provides a good starting point for future development of mechanistic models that directly address the relationships between nutrient input, primary production, sedimentation and hypoxia on the Louisiana Shelf.

Brooks, J., W. Sackett, et al. (1971). "ORGANIC CARBON AS A POLLUTION PARAMETER IN BRAZOS RIVER ESTUARY AND GULF OF MEXICO." Abstracts of Papers of the American Chemical Society(MAR-A): 56-&.

Buesseler, K. O., C. R. Benitez-Nelson, et al. (2006). "An assessment of particulate organic carbon to thorium-234 ratios in the ocean and their impact on the application of Th-234 as a POC flux proxy." Marine Chemistry **100**(3-4): 213-233.

Thorium-234 is increasingly used as a tracer of ocean particle flux, primarily as a means to estimate particulate organic carbon export from the surface ocean. This requires determination of both the Th-234 activity distribution (in order to calculate Th-234 fluxes) and an estimate of the C/Th-234 ratio on sinking particles, to empirically derive C fluxes. In reviewing C/Th-234 variability, results obtained using a single sampling method show the most predictable behavior. For example, in most studies that employ in situ pumps to collect size fractionated particles, C/Th-234 either increases or is relatively invariant with increasing particle size (size classes, 1 to 100s μ m). Observations also suggest that C/Th-234 decreases with depth and can vary significantly between regions (highest in blooms of large diatoms and highly productive coastal settings). Comparisons of C fluxes derived from Th-234 show good agreement with independent estimates of C flux, including mass balances of C and nutrients over appropriate space and time scales (within factors of 2-3). We recommend sampling for C/Th-234 from a standard depth of 100 m, or at least one depth below the mixed layer using either large volume size fractionated filtration to capture the rarer large particles, or a sediment trap or other device to collect sinking particles. We also recommend collection of multiple Th-234 profiles and C/Th-234 samples during the course of longer observation periods to better sample temporal variations in both Th-234 flux and the characteristic of sinking particles. We are encouraged by new technologies which are optimized to more reliably sample truly settling particles, and expect the utility of this tracer to increase, not just for upper ocean C fluxes but for other elements and processes deeper in the water column. (c) 2006 Elsevier B.V. All rights reserved.

Bukaveckas, P. A., D. L. Guelda, et al. (2005). "Effects of point source loadings, sub-basin inputs and longitudinal variation in material retention on C, N and P delivery from the Ohio River basin." Ecosystems **8**(7): 825-840.

Spatial variability in material fluxes within large river basins may arise from point source inputs, variable contributions from sub-basins and longitudinal variation in material transformation and retention. By measuring instantaneous fluxes throughout the Ohio River basin, we were able to draw inferences about the importance of these factors in determining the overall export of C, N and P from the basin. Our study spanned the lower 645 km of the Ohio River and included all tributaries that contributed at least 1% of the volume of the Ohio River at its confluence with the Mississippi. The intensively cultivated northern sub-basin (Wabash River) contributed a large fraction of N and P entering the Ohio River. In the southern sub-basins (Tennessee and Cumberland Rivers), impoundments and less intense cultivation appear to diminish and delay material delivery

particularly with respect to N. The southern rivers account for a proportionately larger fraction of the water entering the Mississippi River during low discharge conditions and this fraction has increased during the past 50 years. The upper portion of the study reach was found to be a net source of CHLa and DOC and a net sink for inorganic N suggesting that this portion of the river provided a generally favorable environment for autotrophic production. Point source loadings of NH₄ were significant inputs to the upper sub-reach but a relatively small component of the overall budget for dissolved inorganic N.

Burdige, D. J. (2005). "Burial of terrestrial organic matter in marine sediments: A re-assessment." Global Biogeochemical Cycles **19**(4).

Calculations based on recent observations indicate that approximately one third of the organic matter presently being buried in marine sediments may be of terrestrial origin, with the majority of this terrestrial organic matter (TOM) burial occurring in muddy, deltaic sediments. These calculations further suggest that the remineralization of terrestrial organic matter in the oceans is also much less efficient than that of marine organic matter. These two underappreciated observations have important implications in terms of our understanding of the controls on the global carbon cycle. From a paleoceanographic perspective, the results presented here also suggest that changes in TOM burial on glacial-interglacial timescales have the potential to impact the global carbon cycle (i.e., atmospheric CO₂ levels).

Burdige, D. J. (2007). "Preservation of organic matter in marine sediments: Controls, mechanisms, and an imbalance in sediment organic carbon budgets?" Chemical Reviews **107**(2): 467-485.

Burnett, W. C., H. Bokuniewicz, et al. (2003). "Groundwater and pore water inputs to the coastal zone." Biogeochemistry **66**(1-2): 3-33.

Both terrestrial and marine forces drive underground fluid flows in the coastal zone. Hydraulic gradients on land result in groundwater seepage near shore and may contribute to flows further out on the shelf from confined aquifers. Marine processes such as tidal pumping and current-induced pressure gradients may induce interfacial fluid flow anywhere on the shelf where permeable sediments are present. The terrestrial and oceanic forces overlap spatially so measured fluid advection through coastal sediments may be a result of composite forcing. We thus define "submarine groundwater discharge" (SGD) as any and all flow of water on continental margins from the seabed to the coastal ocean, regardless of fluid composition or driving force. SGD is typically characterized by low specific flow rates that make detection and quantification difficult. However, because such flows occur over very large areas, the total flux is significant. Discharging fluids, whether derived from land or composed of re-circulated seawater, will react with sediment components. These reactions may increase substantially the concentrations of nutrients, carbon, and metals in the fluids. These fluids are thus a source of biogeochemically important constituents to the coastal ocean. Terrestrially-derived fluids represent a pathway for new material fluxes to the

coastal zone. This may result in diffuse pollution in areas where contaminated groundwaters occur. This paper presents an historical context of SGD studies, defines the process in a form that is consistent with our current understanding of the driving forces as well as our assessment techniques, and reviews the estimated global fluxes and biogeochemical implications. We conclude that to fully characterize marine geochemical budgets, one must give due consideration to SGD. New methodologies, technologies, and modeling approaches are required to discriminate among the various forces that drive SGD and to evaluate these fluxes more precisely.

Cai, W. J., F. Z. Chen, et al. (2006). "Preferential dissolution of carbonate shells driven by petroleum seep activity in the Gulf of Mexico." Earth and Planetary Science Letters **248**(1-2): 227-243.

Authigenic carbonates are common at deep-sea petroleum seeps as a result of excess bicarbonate production during microbial degradation of hydrocarbons coupled to sulfate reduction. Consequently, these seep environments are supersaturated with respect to carbonates. This finding conflicts with taphonomic data that dissolution is the most pervasive mode of shell alteration at seeps. We provide here the first study linking the preservational process with the chemical characterization of the taphonomically-active zone at petroleum seep sites. This characterization is made possible using fine-scale porewater carbonate chemistry data and skeletal material deployed for 8 years at petroleum seep sites in the northwestern Gulf of Mexico. Microelectrode measurements of pH and pCO₂ identify a very restricted zone of CaCO₃ undersaturation immediately below the sediment-water interface in otherwise supersaturated environments (i.e., sandwiched between supersaturated bottom seawater and sediment porewater). This zonation characterizes the taphonomically-active zone, and is a result of a highly compressed redox front between acid-generating aerobic oxidation of reduced chemical species including hydrocarbons, H₂S, and planktonic-and-terrestrial organic carbon and base-generating sulfate reduction coupled to CH₄ oxidation. Porewater geochemistry is spatially variable at seep sites, and produces variable shell-dissolution signatures. Shells deployed at seep sites have moderate to severe dissolution that is consistent with a much higher flux of total dissolved inorganic carbon (DIC) from the porewater to the bottom water. Therefore, a mosaic of preservational conditions is directly related to the spatially and chemically varying taphonomically-active zones found at seep sites. These findings support the variability of carbonate preservation reported for globally-distributed Phanerozoic fossil seeps and the view that data from field taphonomy can significantly upgrade and validate carbonate destruction rates used in geochemical and climatic models. Carbon mass-balance analyses also lead to an important conclusion that carbonate dissolution forms a very important mechanism for benthic carbon recycling, possibly accounting for 50% of the benthic DIC flux to the bottom water in northern Gulf of Mexico petroleum seep sediments. (c) 2006 Elsevier B.V. All rights reserved.

Callaway, J. C., R. D. DeLaune, et al. (1997). "Sediment accretion rates from four

coastal wetlands along the Gulf of Mexico." Journal of Coastal Research **13**(1): 181-191.

Our study of sediment accretion rates from four low tidal-range sites along the Gulf of Mexico does not support previous hypotheses concerning the relationship between tidal range and vertical accretion rates. The addition of our data to an earlier data set decreased the correlation between these variables, and all but one of our low-tidal range sites had positive accretion rates, contradicting previous studies which have predicted that low tidal-range sites would have negative net accretion rates. Additionally, in transects across the marsh, accretion rates decreased from low- to high-marsh stations; however, this appeared to be caused by changes in rates of organic matter accumulation, not mineral matter accumulation, as has been proposed in previous studies. Vertical accretion rates were more strongly correlated with organic matter accumulation rates than mineral matter accumulation rates, confirming previous studies which indicated the important role of sediment organic matter in determining sediment structure. These results do not imply that mineral matter is unimportant in maintaining the elevation of the marsh; mineral matter input affects organic matter production and sediment bulk density. There was little correlation between mineral and organic matter accumulation rates, with average organic matter accumulation rates for each site having little variation compared to the variation in mineral matter accumulation rates. This result supports a previous hypothesis that there may be a limit to annual rates of organic matter accumulation. Finally, the study indicates that the negative net accretion rates documented in Louisiana are not typical of other Gulf coast wetlands.

Carney, R. S. (2005). Zonation of deep biota on continental margins. Oceanography and Marine Biology - an Annual Review, Vol. 43. **43**: 211-+.

Pioneering deep-sea surveys established that the fauna of the continental margins is zoned in the sense that individual species and assemblages occupy restricted depth bands. It has been speculated that the causes of this wide-spread pattern might involve cold temperatures, high pressures and limited foods availability. Increased sampling over the past two decades has confirmed the global presence of depth zonation. Well-defined zonation in the cold polar oceans and the warm Mediterranean indicate that temperature per se may be of less importance on ecological timescales than originally proposed. Strong alternatives are range restriction by pressure and food availability. Understanding of pressure physiology has advanced greatly, and it is to be expected that all deep organisms possess some form of genetic adaptation for pressure tolerance. Since high pressure and low temperatures affect membrane and enzyme systems similarly, combined piezo-thermal thresholds may limit depth ranges. There is a negative, exponential gradient of food availability caused by the decrease in labile carbon influx to bottom. The TROX model linking carbon influx with interstitial oxygen levels has been successful in explaining deep distributions of benthic Foraminifera. and may be more broadly applicable. Current efforts to relate metazoan ranges to food availability are, however, hindered by limited understanding of how organisms recognise and utilise the nutritious content of

detritus. Thus, the exact controls of depth zonation remain conjectural. Zonation studies are gaining in importance due to the increasing availability of deep fauna databases and the need to establish regulatory boundaries. Future studies may benefit from a growing body of biogeographic theory, especially the understanding of bounded domains. It is proposed that continental slope fauna may be more effectively studied if viewed as the overlapping of three components: species extending down from the shelf, species extending up from the abyss and species truly restricted to the slope.

Cavanaugh, J. C., W. B. Richardson, et al. (2006). "Nitrogen dynamics in sediment during water level manipulation on the Upper Mississippi River." River Research and Applications **22**(6): 651-666.

Nitrogen (N) has been linked to increasing eutrophication in the Gulf of Mexico and as a result there is increased interest in managing and improving water quality in the Mississippi River system. Water level reductions, or 'drawdowns', are being used more frequently in large river impoundments to improve vegetation growth and sediment compaction. We selected two areas of the Upper Mississippi River system (Navigation Pool 8 and Swan Lake) to examine the effects of water level drawdown on N dynamics. Navigation Pool 8 experienced summer drawdowns in 2001 and 2002. Certain areas of Swan Lake have been drawn down annually since the early 1970s where as other areas have remained inundated. In the 2002 Pool 8 study we determined the effects of sediment drying and rewetting resulting from water level drawdown on (1) patterns of sediment nitrification and denitrification and (2) concentrations of sediment and surface water total N (TN), nitrate, and ammonium (NH₄⁺). In 2001, we only examined sediment NH₄⁺ and TN. In the Swan Lake study, we determined the long-term effects of water level drawdowns on concentrations of sediment NH₄⁺ and TN in sediments that dried annually and those that remained inundated. Sediment NH₄⁺ decreased significantly in the Pool 8 studies during periods of desiccation, although there were no consistent trends in nitrification and denitrification or a reduction in total sediment N. Ammonium in sediments that have dried annually in Swan Lake appeared lower but was not significantly different from sediments that remain wet. The reduction in sediment NH₄⁺ in parts of Pool 8 was likely a result of increased plant growth and N assimilation, which is then redeposited back to the sediment surface upon plant senescence. Similarly, the Swan Lake study suggested that drawdowns do not result in long term reduction in sediment N. Water level drawdowns may actually reduce water retention time and river-floodplain connectivity, while promoting significant accumulation of organic N. These results indicate that water level drawdowns are probably not an effective means of removing N from the Upper Mississippi River system. Copyright (c) 2006 John Wiley & Sons, Ltd.

Chen, N., T. S. Bianchi, et al. (2003). "Implications for the role of pre- versus post-depositional transformation of chlorophyll-a in the Lower Mississippi River and Louisiana shelf." Marine Chemistry **81**(1-2): 37-55.

Water column particulates and sediments were collected in September 1998 and

July 1999 from the Lower Mississippi River and two shelf sites, an oxic shelf site within the existing plume region and a hypoxic shelf site west of the existing plume. Sediment core samples were collected in April 2000 along a cross-shelf transect that included hypoxic waters. Photosynthetic pigments (chlorophylls and carotenoids) and chlorophyll-a (Chl-a) transformation products in water column particulates and sediments were examined using high performance liquid chromatography (HPLC) on-line photodiode array (PDA) detector and HPLC on-line mass spectrometry (MS). Based on class-specific plant pigment concentrations, diatoms and cyanobacteria were found to be the major sources of organic matter buried in Louisiana (LA) shelf sediments. Pheophytin-a (17.3 +/- 6.3%), pyropheophytin-a (24.6 +/- 8.5%), chlorophyllone-a (9.6 +/- 4.9%), carotenoid chlorin esters (CCEs, 13.7 +/- 5.4%) and sterol chlorin esters (SCEs, 25.5 +/- 8.5%) were the dominant chlorophyll-a transformation products in shelf sediments. The absence of the two grazing biomarkers, CCEs and SCEs, in river sediments suggests that inputs from water column macrozooplankton grazing were not as important in river waters as compared to shelf waters. High concentrations of chlorophyllone-a in river sediments suggest that it was not likely produced through macrozooplankton grazing processes-like CCEs and SCEs. Our results indicate that chlorophyllone-a was likely to be associated with phytoplankton senescence and microbial breakdown of chlorophyll-a. Correlation analyses revealed significant correlations between SCEs, CCEs and pyropheophytin-a in shelf sediments, which indicate that their production in shelf waters was closely coupled to grazing activities on the shelf. Although many of the specific mechanisms of chlorophyll-a decay proposed in this study remain speculative, this work does provide a general foundation, using state-of-the-art analyses of plants pigments, for comparing and contrasting pre- and post-depositional carbon decay pathways in river and shelf environments. (C) 2002 Elsevier Science B.V. All rights reserved.

Chen, N. H., T. S. Bianchi, et al. (2005). "Early diagenesis of chloropigment biomarkers in the lower Mississippi River and Louisiana shelf: implications for carbon cycling in a river-dominated margin." Marine Chemistry **93**(2-4): 159-177.

Sediment core samples were collected from two sites in the lower Mississippi River, an oxic shelf site and a hypoxic shelf site (in September 1998 and July 1999), and from a cross-shelf transect (in April 2000), to examine the differential effects of redox and sedimentation rate on carbon decay dynamics in a river-dominated margin. Downcore distribution of pigments, bulk organic carbon and nitrogen, and radioactive isotopes (Pb-210, Be-7) were used to evaluate the decomposition and preservation of pigments and bulk organic carbon. The distinctly different sedimentary regimes and dynamic nature of the LA shelf limit the application of diagenetic models. Sedimentation processes in the lower Mississippi River and oxic shelf sites were significantly impacted by the river discharge. In areas with low sedimentation, the depth of the surface mixed layer fluctuated with seasonal variation of weather forcing. It was observed that pigment decay rate constants in the mixed layer (7.52 year⁻¹) for chlorophyll-a) were greater than those in the accumulation layer (0.14-0.22 year⁻¹) for

chlorophyll-a) by 1-2 orders of magnitude. This suggests that enhanced decomposition of reactive organic carbon occurred in the mixed layer at locations with low sedimentation rates-due to higher decay rates. Conversely, at locations with high sedimentation rates (>10 cm year⁻¹), the reactive carbon pool was rapidly buried below the mixed layer. The surface mixed layer likely worked as a biogeochemical reactor receiving high inputs of phytodetritus, supported by an active microbial community. We propose that despite the frequency of occurrence of bottom water hypoxia on the Louisiana shelf, sedimentation rate and lability of organic matter are more important in controlling the preservation of organic carbon. (C) 2004 Elsevier B.V. All rights reserved.

Chen, N. H., T. S. Bianchi, et al. (2001). "Historical trends of hypoxia on the Louisiana shelf: application of pigments as biomarkers." Organic Geochemistry **32**(4): 543-561. Increases in the deposition of phytoplankton-derived organic carbon resulting from increases in nutrient inputs through the Mississippi-Atchafalaya system since the early 1950s has been speculated as the primary reason for the occurrence of hypoxic events in this region (Rabalais, N.N., Wiseman, W.J., Turner, R.E., Sen Gupta, B.K., Dortch, Q., 1996. Nutrient changes in the Mississippi river and system responses on the adjacent continental shelf. *Estuaries* 19(2B), 386-407). However, due to the lack of long-term measurements of oxygen in this region it is unclear if hypoxia events occurred prior to anthropogenic inputs of nutrients from the Mississippi river. In this study, we used naturally occurring radionuclides and plant pigment biomarkers to document changes in hypoxia events over the past 100 years. Specifically, we used pigments derived from the anoxygenic phototrophic brown-pigmented green sulfur bacteria *Chlorobium phaeovibroides* and *C. phacobacteroides*. In sediments, at a hypoxic site west of the Mississippi plume, we observed high concentrations (52 nmol/g OC) of bacteriochlorophyll-e along with the specific decay product homologues of bacteriopheophytin-e (15 nmol/g OC). The down-core distribution of bacteriochlorophyll-c and bacteriopheophytin-e homologues (in particular the more stable bacteriopheophytin-e) indicated that the highest concentrations occurred between 1960 and the present, coinciding with increased nutrient loading from the Mississippi river. These bacteriopigments were not detected prior to the early 1900s. These results are consistent with the view that increases in riverine nutrient loadings is likely the major cause of increasing trends in hypoxic events along the Louisiana coast over the past 50 years. (C) 2001 Elsevier Science Ltd. All rights reserved.

Chen, R. F. and G. B. Gardner (2004). "High-resolution measurements of chromophoric dissolved organic matter in the Mississippi and Atchafalaya River plume regions." Marine Chemistry **89**(1-4): 103-125.

Chromophoric dissolved organic matter (CDOM) was measured in the spring and summer in the northern Gulf of Mexico with the ECOShuttle, a towed, instrumented, undulating vehicle. A submersible pump mounted on the vehicle supplied continuously flowing, uncontaminated seawater to online instruments in the shipboard laboratory and allowed discrete samples to be taken for further

analysis. CDOM in the northern Gulf of Mexico was dominated by freshwater inputs from the Mississippi River through the Birdfoot region and to the west by discharge from the Atchafalaya River. CDOM was more extensively dispersed in the high-flow period in the spring but in both time periods was limited by stratification to the upper 12 m or so. Thin, subsurface CDOM maxima were observed below the plume during the highly stratified summer period but were absent in the spring. However, there was evidence of significant in situ biological production of CDOM in both seasons. The Mississippi River freshwater end member was similar in spring and summer, while the Atchafalaya end member was significantly higher in the spring. In both time periods, the Atchafalaya was significantly higher in CDOM and dissolved organic carbon (DOC) than the Mississippi presumably due to local production and exchange within the coastal wetlands along the lower Atchafalaya which are absent along the lower Mississippi. Nearshore waters may also have higher CDOM due to outwelling from coastal wetlands. High-resolution measurements allow the differentiation of various water masses and are indicative of rapidly varying (days to weeks) source waters. Highly dynamic but conservative mixing between various freshwater and marine end members apparently dominates CDOM distributions in the area with significant in situ biological inputs (bacterial degradation of phytoplankton detritus), evidence of flocculation, and minor photobleaching effects also observed. It is clear that high-resolution measurements and adaptive sampling strategies allow a more detailed examination of the processes that control CDOM distributions in river-dominated systems. (C) 2004 Elsevier B.V. All rights reserved.

Chen, X., S. E. Lohrenz, et al. (2000). "Distribution and controlling mechanisms of primary production on the Louisiana-Texas continental shelf." Journal of Marine Systems **25**(2): 179-207.

The northwest (NW) Gulf of Mexico is marked by strong seasonal patterns in regional and mesoscale circulation and variable effects of riverine/estuarine discharge, which influence distributions of nutrients, phytoplankton biomass and primary production. During a series of five cruises in the NW Gulf of Mexico in 1993 and 1994, an extensive data set was collected including nutrients, phytoplankton biomass (chlorophyll a), and photosynthesis-irradiance (P-E) parameters. Primary production was estimated using P-E parameters in conjunction with profiles of biomass and irradiance. Relatively high biomass and primary production were observed in inner shelf waters during spring conditions of high river discharge. This was attributed to the retention of biomass and nutrients on the shelf by the combination of high river outflow and a westward flow along the inner shelf with consequent onshore Ekman component. During summer, when surface currents shifted towards the north and east, values of nutrients, biomass and primary production were relatively high east of Galveston Bay and decreased outward from the coast. This pattern was apparently a consequence of nutrient inputs from riverine, upwelling and benthic sources. Nutrients, biomass and productivity in the western portion of the study area in summer were generally lower as a result of the upcoast Row of oligotrophic

offshore water. Inter-annual variability was observed between November 1993 and 1994 with higher biomass and productivity occurring in November 1993. This was partially attributed to higher river discharge prior to November 1993, retention of biomass and nutrients by the downcoast flow along the inner shelf, and possibly, injection of nutrients onto the shelf at the shelf break. Our findings demonstrate that the interaction of circulation and availability of Light and nutrients are largely responsible for variations in primary production. Nitrogen appeared to be the primary limiting nutrient, however, a potential for phosphate limitation was also observed particularly during periods of higher river discharge. Light availability was a critical variable during the fall and winter months, when higher primary production was restricted to shallow waters where vertical mixing was constrained by bottom topography. In deep waters, counteractive changes in nutrient and light availability apparently resulted in minor temporal variation between seasons. The annual carbon production in the Louisiana-Texas (LATEX) continental shelf region was estimated to be $159 \text{ g C m}^{-2} \text{ year}^{-1}$, which is within the range of prior estimates for this region. Given that the area of the study region was approximately $140,000 \text{ km}^2$, this would be equivalent to an areal carbon production of about 22.2 million metric tons. (C) 2000 Elsevier Science B.V. All rights reserved.

Chen, Y., R. Matsumoto, et al. (2007). "Methane-derived authigenic carbonates from the northern Gulf of Mexico - MD02 cruise." Journal of Geochemical Exploration **95**(1-3): 1-15.

Authigenic carbonates were sampled in piston cores collected from both the Tunica Mound and the Mississippi Canyon area on the continental slope of the northern Gulf of Mexico during a Marion Dufresne cruise in July 2002. The carbonates are present as hardgrounds, porous crusts, concretions or nodules and shell fragments with or without carbonate cements. Carbonates occurred at gas venting sites which are likely to overlie gas hydrates bearing sediments. Electron microprobe, X-ray diffraction (XRD) and thinsection investigations show that these carbonates are high-Mg calcite (6-21 Mol% MgCO_3), with significant presence of framboidal pyrite. All carbonates are depleted in C-13 ($\delta \text{C-13} = -61.9$ to -31.5 parts per thousand PDB) indicating that the carbon is derived mainly from anaerobic methane oxidation (AMO). Age estimates based on C-14 dating of shell fragments and on regional sedimentation rates indicate that these authigenic carbonates formed within the last 1000 yr in the Mississippi Canyon and within 5500 yr at the Tunica Mound. The oxygen isotopic composition of carbonates ranges from +3.4 to +5.9 parts per thousand PDB. Oxygen isotopic compositions and Mg^{2+} contents of carbonates, and present in-situ temperatures of bottom seawater/sediments, show that some of these carbonates, especially from a core associated with underlying massive gas hydrates precipitated in or near equilibrium with bottom-water. On the other hand, those carbonates more enriched in O-18 are interpreted to have precipitated from O-18-rich fluids which are thought to have been derived from the dissociation of gas hydrates. The dissociation of gas hydrates in the northern Gulf of Mexico within the last 5500 yr may be caused by nearby salt movement and related brines. (C) 2007 Elsevier

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Chinleo, G. and R. Benner (1992). "ENHANCED BACTERIOPLANKTON PRODUCTION AND RESPIRATION AT INTERMEDIATE SALINITIES IN THE MISSISSIPPI RIVER PLUME." Marine Ecology-Progress Series **87**(1-2): 87-103.

Bacterial abundance and production (thymidine and leucine incorporation) were measured along a salinity gradient from the Mississippi River (0 parts per thousand) to the open waters of the Gulf of Mexico (36 parts per thousand) during July-August 1990 and February 1991. Bacterial production in surface waters was maximal at intermediate salinities (15 to 30 parts per thousand). Nutrient enrichment experiments suggested that bacterial growth near the outflow of the river was C limited whereas bacteria in plume waters of intermediate salinities were P and N limited. Rates of plankton community oxygen demand measured during winter were also maximal at intermediate salinities indicating an area of increased heterotrophic activity. The oxygen demand associated with heterotrophic bacterioplankton activity during summer was an important factor leading to hypoxic conditions in bottom waters of the Louisiana continental shelf. In summer, bacterial abundance and production ranged from 0.25 to 3.34×10^9 cells l⁻¹ and from 4 to 90 $\mu\text{g C l}^{-1} \text{d}^{-1}$, respectively. In winter, the corresponding ranges were 0.36 to 1.09×10^9 cells l⁻¹ and 3 to 20 $\mu\text{g C l}^{-1} \text{d}^{-1}$. Depth-integrated bacterial production on the Louisiana shelf decreased from 443 \pm 144 $\text{mg C m}^{-2} \text{d}^{-1}$ in summer to 226 \pm 124 $\text{mg C m}^{-2} \text{d}^{-1}$ in winter. Using empirically-derived bacterial growth efficiency values of 19 and 29 %, we estimated that bacterial production in summer could be supported by 10 to 58 % of phytoplankton production. In winter, the amount of carbon needed to support bacterial production exceeded phytoplankton production suggesting that bacterial growth during this season was heavily dependent on riverine sources of organic matter.

Chmura, G. L., S. C. Anisfeld, et al. (2003). "Global carbon sequestration in tidal, saline wetland soils." Global Biogeochemical Cycles **17**(4).

[1] Wetlands represent the largest component of the terrestrial biological carbon pool and thus play an important role in global carbon cycles. Most global carbon budgets, however, have focused on dry land ecosystems that extend over large areas and have not accounted for the many small, scattered carbon-storing ecosystems such as tidal saline wetlands. We compiled data for 154 sites in mangroves and salt marshes from the western and eastern Atlantic and Pacific coasts, as well as the Indian Ocean, Mediterranean Ocean, and Gulf of Mexico. The set of sites spans a latitudinal range from 22.4degreesS in the Indian Ocean to 55.5degrees N in the northeastern Atlantic. The average soil carbon density of mangrove swamps (0.055 \pm 0.004 g cm^{-3}) is significantly higher than the salt marsh average (0.039 \pm 0.003 g cm^{-3}). Soil carbon density in mangrove swamps and *Spartina patens* marshes declines with increasing average annual temperature, probably due to increased decay rates at higher temperatures. In contrast, carbon sequestration rates were not significantly different between mangrove swamps and salt marshes. Variability in sediment accumulation rates

within marshes is a major control of carbon sequestration rates masking any relationship with climatic parameters. Globally, these combined wetlands store at least 44.6 Tg C yr⁻¹) and probably more, as detailed areal inventories are not available for salt marshes in China and South America. Much attention has been given to the role of freshwater wetlands, particularly northern peatlands, as carbon sinks. In contrast to peatlands, salt marshes and mangroves release negligible amounts of greenhouse gases and store more carbon per unit area.

Clark, C. D., W. T. Hiscock, et al. (2004). "CDOM distribution and CO₂ production on the southwest Florida shelf." Marine Chemistry **89**(1-4): 145-167.

Partial pressures of carbon dioxide (pCO₂) were measured in river and coastal waters on two cruises in November 1999 and June 2000 on the Southwest Florida Shelf. Supersaturation with respect to the atmosphere was observed for most river and nearshore waters in November 1999. pCO₂ ranged from 403 μatm in the Gulf of Mexico to 1280 μatm in the Shark River. The coastal waters of the Southwest Florida Shelf had unusually low salinities at this time due to high inputs of freshwater runoffs after Hurricane Irene. In general, pCO₂ levels decreased with increasing salinity, but at different gradients for the different river systems. In June 2000, salinity gradients were considerably reduced during this drought year, with hypersalinity indicating reduced freshwater inputs. However, high pCO₂ levels were still observed in and near the mouth of the Shark River (pCO₂ = 383-1280 μatm). A positive correlation of pCO₂ levels with colored dissolved organic matter (CDOM) and chlorophyll was observed in all systems examined. CO₂ in natural waters may be produced from the photochemical degradation of CDOM, microbial respiration or via shifts in the carbonate equilibrium. Some evidence for a small contribution from photochemical production was observed in the Shark River mouth in a dry season diel study, but not in the wet season. Differences between the rivers are primarily attributed to the significantly higher total alkalinity and lower pH values in the Shark River, and associated higher pCO₂ levels. In general, spatial variability in pCO₂ is dominated by the chemical characteristics of the river inputs, with temporal variability modulated by changes in pH, photochemical production in low flow seasons and draw down by primary production. (C) 2004 Elsevier B.V. All rights reserved.

Codispoti, L. A. (2007). "An oceanic fixed nitrogen sink exceeding 400 Tg N a⁻¹ vs the concept of homeostasis in the fixed-nitrogen inventory." Biogeosciences **4**(2): 233-253. Measurements of the NZ produced by denitrification, a better understanding of non-canonical pathways for NZ production such as the anammox reaction, better appreciation of the multiple environments in which denitrification can occur (e.g. brine pockets in ice, within particles outside of suboxic water, etc.) suggest that it is unlikely that the oceanic denitrification rate is less than 400 Tg N a⁻¹. Because this sink term far exceeds present estimates for nitrogen fixation, the main source for oceanic fixed-N, there is a large apparent deficit (similar to 200 Tg N a⁻¹) in the oceanic fixed-N budget. The size of the deficit appears to conflict with apparent constraints of the atmospheric carbon dioxide and

sedimentary delta N-15 records that suggest homeostasis during the Holocene. In addition, the oceanic nitrate/phosphate ratio tends to be close to the canonical Redfield biological uptake ratio of 16 (by N and P atoms) which can be interpreted to indicate the existence of a powerful feed-back mechanism that forces the system towards a balance. The main point of this paper is that one cannot solve this conundrum by reducing the oceanic sink term. To do so would violate an avalanche of recent data on oceanic denitrification. A solution to this problem may be as simple as an upwards revision of the oceanic nitrogen fixation rate, and it is noted that most direct estimates for this term have concentrated on nitrogen fixation by autotrophs in the photic zone, even though nitrogen fixing genes are widespread. Another simple explanation may be that we are simply no longer in the Holocene and one might expect to see temporary imbalances in the oceanic fixed-N budget as we transition from the Holocene to the Anthropocene in line with an apparent denitrification maximum during the Glacial-Holocene transition. Other possible full or partial explanations involve plausible changes in the oceanic nitrate/phosphate and N/C ratios, an oceanic phosphorus budget that may also be in deficit, and oscillations in the source and sink terms that are short enough to be averaged out in the atmospheric and geologic records, but which could, perhaps, last long enough to have significant impacts.

Coffin, R. B. and L. A. Cifuentes (1999). "Stable isotope analysis of carbon cycling in the Perdido Estuary, Florida." *Estuaries* **22**(4): 917-926.

Stable carbon isotope ($\delta^{13}\text{C}$) analysis was used in the Perdido Estuary, Florida U.S. to determine the predominant carbon source that supports the bacterial assemblage. Stable carbon isotope values were measured in the suspended particulate matter (SPM), dissolved organic and inorganic matter, and bacteria. Stable nitrogen isotope ($\delta^{15}\text{N}$) ratios were measured in SPM and nitrate to assist in understanding carbon cycling through the estuary. Analyses were conducted on samples from riverine, coastal, and anthropogenic sources and compared with samples from the bay. Stable isotope ratio analysis was coupled with estimates of mixing of riverine and coastal waters into the bay. Preliminary observation of the $\delta^{13}\text{C}$ data indicates that terrestrial organic matter is the primary carbon source that is assimilated by bacteria in the ecosystem. Stable isotope data from carbon and nitrogen pools in combination with analysis of estuarine current velocities indicates that primary production is an important factor in the carbon cycle. This study demonstrates the importance of stable isotope analysis of multiple carbon and nitrogen pools to assess sources and cycling of organic matter.

Conmy, R. N., P. G. Coble, et al. (2004). "Optical properties of colored dissolved organic matter in the Northern Gulf of Mexico." *Marine Chemistry* **89**(1-4): 127-144.

Variations in the concentration and inherent optical properties of colored dissolved organic matter (CDOM) in river-dominated margins provide information on the cycling of carbon and its chemical composition. Large-scale temporal and spatial variability in CDOM concentration and optical properties were observed in

the Northern Gulf of Mexico in June of 2000 and April of 2001. Terrestrial CDOM from the Mississippi and Atchafalaya Rivers dominates the region. Although the primary factor controlling CDOM in this region is the quantity of fresh water runoff, strong regional variability in fresh water sources also plays a major role. Physical complexity due to changes in circulation patterns, volume of river flow and multiple river sources makes observation of biological and photochemical effects challenging in this region. We have used two approaches to distinguish between source and transformation effects: mixing models, which include the concentration and inherent optical properties, of CDOM from discrete samples, and high-resolution three-dimensional mapping of multi-spectral fluorescence. (C) 2004 Elsevier B.V. All rights reserved.

Copard, Y., P. Amiotte-Suchet, et al. (2007). "Storage and release of fossil organic carbon related to weathering of sedimentary rocks." Earth and Planetary Science Letters **258**(1-2): 345-357.

The biogeochemical carbon cycle, which plays an undeniable role in global climate change, is defined both by the size of carbon reservoirs (such as the atmosphere, biomass, soil and bedrock) and the exchange between them of various mineral and organic carbon forms. Among these carbon forms, fossil organic carbon (FOC) (i.e., the ancient organic matter stored in sedimentary rocks) is widely observed in modern environments but is not included in the supergene carbon budget. Using a digitized map of the world and an existing model of CO₂ consumption associated with rock weathering, we establish the global distribution of FOC stored in the first meter of sedimentary rocks and a first estimation of annual FOC delivery to the modern environment resulting from chemical weathering of these rocks. Results are given for the world's 40 major river basins and extended to the entire continental surface. With a mean value of $100 \cdot 10^9$ t, mainly controlled by shale distribution, the global FOC stock is significant and comparable to that of soil organic carbon ($1500 \cdot 10^9$ t). The annual chemical delivery of FOC, estimated at $43 \cdot 10^6$ t yr⁻¹ and controlled by the areal distribution of shales and runoff is of the same order of magnitude as the FOC output flux to oceans. Chemical weathering of bedrock within the Amazon basin produces one-quarter of the total global flux of FOC derived from chemical weathering, and thus is expected to govern FOC release on a global scale. These results raise important questions concerning the role of FOC in the modern carbon cycle as well as the origin and the budget of carbon in soils and rivers. (C) 2007 Elsevier B.V. All rights reserved.

Corbett, D. R., B. McKee, et al. (2006). "Nature of decadal-scale sediment accumulation on the western shelf of the Mississippi River delta." Continental Shelf Research **26**(17-18): 2125-2140.

Sediment delivered to coastal systems by rivers ($15 \cdot 10^9$ tons) plays a key role in the global carbon and nutrient cycles, as deltas and continental shelves are considered to be the main repositories of organic matter in marine sediments. The Mississippi River, delivering more than 60% of the total dissolved and suspended materials from the conterminous US, dominates coastal and margin

processes in the northern Gulf of Mexico. Draining approximately 41% of the conterminous US, the Mississippi and Atchafalaya river system deliver approximately 2×10^8 tons of suspended matter to the northern Gulf shelf each year. Unlike previous work, this study provides a comprehensive evaluation of sediment accumulation covering majority of the shelf (< 150 m water depth) west of the Mississippi Delta from 92 cores collected throughout the last 15 years. This provides a unique and invaluable data set of the spatial and modern temporal variations of the sediment accumulation in this dynamic coastal environment. Three types of Pb-210 profiles were observed from short cores (15-45 cm) collected on the shelf. Proximal to Southwest Pass in 30-100 m water depths, non-steady-state profiles were observed indicating rapid accumulation. Sediment accumulation rates in this area are typically $> 2.5 \text{ cm yr}^{-1}$ ($> 1.8 \text{ g cm}^{-2} \text{ yr}^{-1}$). Kasten cores (similar to 200 cm in length) collected near Southwest Pass also indicate rapid deposition ($> 4 \text{ cm yr}^{-1}$; $> 3 \text{ g cm}^{-2} \text{ yr}^{-1}$) on a longer timescale than that captured in the box cores. Near shore (< 20 m), profiles are dominated by sediments reworked by waves and currents with no accumulation (the exception is an area just south of Barataria Bay where accumulation occurs). The remainder of the shelf (distal of Southwest Pass) is dominated by steady-state accumulation beneath a similar to 10-cm thick mixed layer. Sediment accumulation rates for the distal shelf are typically $< 0.7 \text{ cm yr}^{-1}$ ($< 0.5 \text{ g cm}^{-2} \text{ yr}^{-1}$). A preliminary sediment budget based on the distribution of Pb-210 accumulation rates indicates that 40-50% of the sediment delivered by the river is transported out of the study region. Sediment is moved to distal regions of the shelf/slope through two different mechanisms. Along-isobath sediment movement occurs by normal resuspension processes west of the delta, whereas delivery of sediments south and southwest of the delta may be also be influenced by mass movement events on varying timescales. (c) 2006 Elsevier Ltd. All rights reserved.

Corbett, D. R., B. McKee, et al. (2004). "An evaluation of mobile mud dynamics in the Mississippi River deltaic region." *Marine Geology* **209**(1-4): 91-112.

Large rivers are the primary interface between terrestrial and ocean environments. A relatively small number of rivers account for a disproportionate amount of the freshwater and suspended materials that are delivered to the coastal ocean. Sediment delivery to these coastal systems plays a key role in the global carbon cycle since deltas and continental shelves are considered to be the main repositories of organic carbon in marine sediments. Particulate material in these environments are typically deposited and resuspended several times before permanent accumulation or transport off the shelf. This sediment cycling is an important component influencing biogeochemical processes that occur in coastal environments. During two cruises in April and October 2000 on the shelf adjacent to the Mississippi River, water and sediment samples were collected for analysis of suspended solids and particle reactive radionuclides (Pb-210, Cs-137, Be-7 and Th-234) to evaluate the transport and fate of terrestrial and marine material. A comparison of the distribution of these tracers provides insight about the pathways and residence times of particulate materials on the shelf.

Inventories of these short-lived radiotracers showed variations of more than two orders of magnitude, indicating dramatic variations in sediment deposition between sampling events. Short-lived radiotracers indicate that river-borne materials are transported less than similar to 30 km from the river mouth before initial deposition. However, seasonal variations in Be-7 and Cs-137 indicate significant remobilization of sediment and potential export of sediment out of the study area during the high energy (e.g., wind/wave) winter months. In addition, depth profiles of Be-7 and excess Th-234 indicate sediment deposition rates between 0.8 and 3.9 cm month⁽⁻¹⁾ (0.4-2.1 g cm⁽⁻²⁾ month⁽⁻¹⁾) at two shelf locations (near river and open shelf environments). These rates are much greater than those observed on decadal time scales (1.3-2.0 cm year⁽⁻¹⁾ or 0.6-1.5 g cm⁽⁻²⁾ year⁽⁻¹⁾) via Pb-210 at the same sites. This further substantiates active sediment reworking and potential export off the shelf as has been observed in other river-dominated ocean margins. (C) 2004 Elsevier B.V. All rights reserved.

Cotner, J. B. and W. S. Gardner (1993). "HETEROTROPHIC BACTERIAL MEDIATION OF AMMONIUM AND DISSOLVED FREE AMINO-ACID FLUXES IN THE MISSISSIPPI RIVER PLUME." Marine Ecology-Progress Series **93**(1-2): 75-87.

Bacterial nitrogen regeneration processes are an important source of nitrogen in the most productive regions of the Mississippi River plume (Gulf of Mexico). We examined bacterial growth rates, ammonium regeneration rates, and labile dissolved organic carbon/nitrogen fluxes on 2 cruises in the Mississippi River plume. In summer, surface water bacterial production rates, ammonium regeneration rates, and amino acid turnover rates were higher at intermediate salinities than corresponding rates at the river mouth or in high salinity waters. In winter, surface amino acid turnover rates were highest in the river but growth rates were highest in the plume and ammonium regeneration rates were similar at all sites. Regeneration rates in the plume were an order of magnitude greater in the summer than in the winter. A significant proportion of the bacterial nitrogen demand may be provided by amino acid fluxes in summer, especially in the plume. Measurements of NH₄ regeneration after manipulating bacterial abundances suggest that heterotrophic bacteria contributed a variable proportion (7 to 50 %) of total N-regeneration in summer and that dissolved free amino acids could be a major substrate for ammonium regeneration. Depth profiles, spatial distributions, and seasonal differences in ammonium regeneration rates imply that the fastest regeneration rates occur spatially and temporally where primary production is the greatest.

Dagg, M., R. Benner, et al. (2004). "Transformation of dissolved and particulate materials on continental shelves influenced by large rivers: plume processes." Continental Shelf Research **24**(7-8): 833-858.

The world's ten largest rivers transport approximately 40% of the fresh water and particulate materials entering the ocean. The impact of large rivers is important on a regional/continental scale (e.g. the Mississippi drains similar to 40% of the conterminous US and carries approximately 65% of all the suspended solids and dissolved solutes that enter the ocean from the US) and on a global scale (e.g.

the Amazon River annually supplies approximately 20% of all the freshwater that enters the ocean; e.g. approximately 85% of all sedimenting organic carbon in the ocean accumulates in coastal margin regions). River plume processes are affected by a suite of complex factors that are not fully understood. It is clear however, that the composition, concentration and delivery of terrestrial materials by large rivers cannot be understood by simply scaling up the magnitudes and impacts of dominant processes in smaller rivers. Because of high rates of particulate and water discharge, the estuarine processes associated with major rivers usually take place on the adjacent continental shelf instead of in a physically confined estuary. This influences the magnitude and selectivity of processes that transform, retain or export terrestrial materials. Buoyancy is a key mediating factor in transformation processes in the coastal margin. In this paper we review and synthesize Current understanding of the transformation processes of dissolved and particulate organic and inorganic materials associated with large river (buoyant) plumes. Chemical and biological activities are greatly enhanced by the changed physical and optical environment within buoyant plumes. Time and space scales over which these transformation processes occur vary greatly, depending on factors such as scales of discharge, suspended sediment loads, light and temperature. An adequate understanding of transformation processes in these highly dynamic, buoyancy-driven systems is lacking. In this paper, we review the biogeochemical processes that occur in large river plumes. (C) 2004 Elsevier Ltd. All rights reserved.

Dagg, M. J., J. W. Ammerman, et al. (2007). "A review of water column processes influencing hypoxia in the northern Gulf of Mexico." Estuaries and Coasts **30**(5): 735-752.

In this review, we use data from field measurements of biogeochemical processes and cycles in the Mississippi River plume and in other shelf regions of the northern Gulf of Mexico to determine plume contributions to coastal hypoxia. We briefly review pertinent findings from these process studies, review recent mechanistic models that synthesize these processes to address hypoxia-related issues, and reinterpret current understanding in the context of these mechanistic models. Some of our conclusions are that both nitrogen and phosphorus are sometimes limiting to phytoplankton growth; respiration is the main fate of fixed carbon in the plume, implying that recycling is the main fate of nitrogen; decreasing the river nitrate loading results in less than a 1:1 decrease in organic matter sinking from the plume; and sedimenting organic matter from the Mississippi River plume can only fuel about 23% of observed coastal hypoxia, suggesting significant contributions from the Atchafalaya River and, possibly, coastal wetlands. We also identify gaps in our knowledge about controls on hypoxia, and indicate that some reinterpretation of our basic assumptions about this system is required. There are clear needs for improved information on the sources, rates, and locations of organic matter sedimentation; for further investigation of internal biogeochemical processes and cycling; for improved understanding of the rates of oxygen diffusion across the pycnocline; for identification and quantification of other sources of organic matter fueling hypoxia

or other mechanisms by which Mississippi River derived organic matter fuels hypoxia; and for the development of a fully coupled physical-biogeochemical model.

Dagg, M. J., T. S. Bianchi, et al. (2005). "Biogeochemical characteristics of the lower Mississippi River, USA, during June 2003." Estuaries **28**(5): 664-674.

During June 2003, a period of midlevel discharge ($17,400 \text{ m}^3 \text{ s}^{-1}$), a parcel of water in the lower Mississippi River was sampled every 2 h during its 4-d transit from river km 362 near Baton Rouge to km 0 at Head of Passes, Louisiana, United States. Properties measured at the surface during each of the 48 stations were temperature, salinity, dissolved organic carbon (DOC), total dissolved nitrogen, dissolved macronutrients ($\text{NO}_3 + \text{NO}_2$, PO_4 , Si(OH)_4), chlorophyll a (chl a; three size fractions: $< 5 \mu\text{m}$, $5\text{-}20 \mu\text{m}$, and $> 20 \mu\text{m}$), pigment composition by HPLC, total suspended matter (TSM), particulate organic carbon (POC), and particulate nitrogen (PN). Air-water CO_2 flux was calculated from surface water dissolved inorganic carbon and pH. During the 4d transit, large particles appeared to be settling out of the surface water. Concentrations of chl a containing particles $> 20 \mu\text{m}$ declined 37%, TSM declined 43%, POC declined 42% and PN declined 57%. Concentrations of the smaller chl a containing particles did not change suggesting only large particulate materials were settling. There was no measurable loss of dissolved NO_3 , PO_4 , or Si(OH)_4 , consistent with the observation that chl a did not increase during the 4-d transit. DOC declined slightly (3%). These data indicate there was little autotrophic or heterotrophic activity in the lower Mississippi River at this time, but the system was slightly net heterotrophic.

Dalzell, B. J., T. R. Filley, et al. (2005). "Flood pulse influences on terrestrial organic matter export from an agricultural watershed." Journal of Geophysical Research-Biogeosciences **110**(G2).

[1] Riverine export of terrestrial organic carbon (TOC) plays an important role in the global C cycle through influences on coastal productivity, sedimentary preservation, and CO_2 efflux. In order to examine the influence of hydrologic variability and upland processes on TOC export from a midwestern agricultural watershed, we applied lignin phenol and stable carbon isotope analyses to assess quantity, source, and relative degradation state of TOC in soils, sediments, and size-fractionated aquatic OC from stream water. Flood conditions exported 90 times more dissolved organic carbon (DOC) than baseflow owing to increases in both discharge and concentration, indicating mobilization of additional DOC pools. These observations are supported by increased TOC contributions to aquatic OC during flooding. Furthermore, stable carbon isotope values show that OC exported during flooding is enriched in C-4-derived C by up to 38% (for high molecular weight DOC) with respect to baseflow, indicating different TOC sources are mobilized dependant on hydrologic conditions. Lignin phenols isolated from the colloid size fraction show progressive increases in the ratio of carboxylic acid to aldehyde functional groups (a measure of relative degradation state) with distance downstream suggesting selective partitioning to

mineral surfaces and/or degradation to this size fraction. This study shows that TOC quantity, source, and relative degradation state can change dependant on hydrologic conditions and in-stream transport in a small agricultural watershed. Moreover, these results are important in showing variability in TOC source and chemistry exported from headwater systems that might otherwise not be detected in studies of larger rivers.

Deegan, L. A. (1993). "NUTRIENT AND ENERGY-TRANSPORT BETWEEN ESTUARIES AND COASTAL MARINE ECOSYSTEMS BY FISH MIGRATION." Canadian Journal of Fisheries and Aquatic Sciences **50**(1): 74-79.

Biomass accumulation and changes in body energy and nutrient (carbon, nitrogen, and phosphorus) composition were evaluated relative to the migration pattern of gulf menhaden (*Brevoortia patronus*) to determine if biotic transport by fish is an important source of energy and nutrients to coastal marine ecosystems. Gulf menhaden transported significant quantities of energy, C, N, and P from a Louisiana estuary to the nearshore Gulf of Mexico. Transport was always out of the estuary to the marine system, although the magnitude depended on the balance between growth and mortality rates and abundance of fish. Average export per year was 38 g biomass, 930 kJ, 22.5 g C, 3.1 g N, and 0.9 g P.m⁻² out of estuaries. This is roughly 5-10% of the total primary production of these estuarine areas. N and P export by fish is of the same magnitude as passive waterborne export; however, it is higher quality. This indicates that fish migration can play an important role in exporting the productivity of estuaries to coastal marine ecosystems.

Del Castillo, C. E. and R. L. Miller (2008). "On the use of ocean color remote sensing to measure the transport of dissolved organic carbon by the Mississippi River Plume." Remote Sensing of Environment **112**(3): 836-844.

We investigated the use of ocean color remote sensing to measure the transport of dissolved organic carbon (DOC) by the Mississippi River to the Gulf of Mexico. From 2000 to 2005 we recorded surface measurements of DOC, colored dissolved organic matter (CDOM), salinity, and water-leaving radiances during five cruises to the Mississippi River Plume. These measurements were used to develop empirical relationships to derive DOC, CDOM, and salinity from monthly composites of SeaWiFS imagery collected from 1998 through 2005. We compared our remote sensing estimates of river flow and DOC transport with data collected by the United States Geological Survey (USGS) from 1998 through 2005. Our remote sensing estimates of river flow and DOC transport correlated well (r^2 similar to 0.70) with the USGS data. Our remote sensing estimates and USGS field data showed low variability in DOC concentrations in the river end-member (7-11%), and high seasonal variability in river flow (similar to 50%). Therefore, changes in river flow control the variability in DOC transport, indicating that the remote sensing estimate of river flow is the most critical element of our DOC transport measurement. We concluded that it is possible to use this method to estimate DOC transport by other large rivers if there are data on the relationship between CDOM, DOC, and salinity in the river plume. (C)

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Desantis, L. R. G., S. Bhotika, et al. (2007). "Sea-level rise and drought interactions accelerate forest decline on the Gulf Coast of Florida, USA." Global Change Biology **13**(11): 2349-2360.

Sea-level rise threatens low-lying coastal ecosystems globally. In Florida, USA, salinity stress due to increased tidal flooding contributes to the dramatic and well documented decline of species-rich coastal forest areas along the Gulf of Mexico. Here, we present the results of a study of coastal forest stand dynamics in thirteen 400 m² plots representing an elevation gradient of 0.58-1.1 m affected by tidal flooding and rising sea levels. We extended previously published data from 1992-2000 to 2005 to quantify the full magnitude of the 1998-2002 La Nina-associated drought. Populations of the dominant tree species, *Sabal palmetto* (cabbage palm), declined more rapidly during 2000-2005 than predicted from linear regressions based on the 1992-2000 data. Dramatic increases in *Juniperus virginiana* (Southern red cedar) and *S. palmetto* mortality during 2000-2005 as compared with 1995-2000 are apparently due to the combined effects of a major drought and ongoing sea-level rise. Additionally, coastal forest stands continued to decline in species richness with increased tidal flooding frequency and decreasing elevation. Stable isotope (H, O) analyses demonstrate that *J. virginiana* accesses fresher water sources more than *S. palmetto*. Carbon isotopes reveal increasing delta C-13 enrichment of *S. palmetto* and *J. virginiana* with increased tidal flooding and decreased elevation, demonstrating increasing water stress in both species. Coastal forests with frequent tidal flooding are unable to support species-rich forests or support regeneration of the most salt-tolerant tree species over time. Given that rates of sea-level rise are predicted to increase and periodic droughts are expected to intensify in the future due to global climate change, coastal forest communities are in jeopardy if their inland retreat is restricted.

Dickens, G. R. (2003). "Rethinking the global carbon cycle with a large, dynamic and microbially mediated gas hydrate capacitor." Earth and Planetary Science Letters **213**(3-4): 169-183.

Prominent negative delta(13)C excursions characterize several past intervals of abrupt (< 100 kyr) environmental change. These anomalies, best exemplified by the > 2.5 parts per thousand drop across the Paleocene/Eocene thermal maximum (PETM) ca. 55.5 Ma, command our attention because they lack explanation with conventional models for global carbon cycling. Increasingly, Earth scientists have argued that they signify massive release of CH₄ from marine gas hydrates, although typically without considering the underlying process or the ensuing ramifications of such an interpretation. At the most basic level, a large, dynamic 'gas hydrate capacitor' stores and releases C-13-depleted carbon at rates linked to external conditions such as deep ocean temperature. The capacitor contains three internal reservoirs: dissolved gas, gas hydrate, and free gas. Carbon enters and leaves these reservoirs through microbial decomposition of organic matter, anaerobic oxidation of CH₄ in shallow

sediment, and seafloor gas venting; carbon cycles between these reservoirs through several processes, including fluid flow, precipitation and dissolution of gas hydrate, and burial. Numerical simulations show that simple gas hydrate capacitors driven by inferred changes in bottom water warming during the PETM can generate a global VC excursion that mimics observations. The same modeling extended over longer time demonstrates that variable CH₄ fluxes to and from gas hydrates can partly explain other delta(13)C excursions, rapid and slow, large and small, negative and positive. Although such modeling is rudimentary (because processes and variables in modern and ancient gas hydrate systems remain poorly constrained), acceptance of a vast, externally regulated gas hydrate capacitor forces us to rethink VC records and the operation of the global carbon cycle throughout time. (C) 2003 Elsevier B.V. All rights reserved.

Dodds, W. K., E. Marti, et al. (2004). "Carbon and nitrogen stoichiometry and nitrogen cycling rates in streams." *Oecologia* **140**(3): 458-467.

Stoichiometric analyses can be used to investigate the linkages between N and C cycles and how these linkages influence biogeochemistry at many scales, from components of individual ecosystems up to the biosphere. N-specific NH₄⁺ uptake rates were measured in eight streams using short-term N-15 tracer additions, and C to N ratios (C:N) were determined from living and non-living organic matter collected from ten streams. These data were also compared to previously published data compiled from studies of lakes, ponds, wetlands, forests, and tundra. There was a significant negative relationship between C:N and N-specific uptake rate; C:N could account for 41% of the variance in N-specific uptake rate across all streams, and the relationship held in five of eight streams. Most of the variation in N-specific uptake rate was contributed by detrital and primary producer compartments with large values of C:N and small values for N-specific uptake rate. In streams, particulate materials are not as likely to move downstream as dissolved N, so if N is cycling in a particulate compartment, N retention is likely to be greater. Together, these data suggest that N retention may depend in part on C:N of living and non-living organic matter in streams. Factors that alter C:N of stream ecosystem compartments, such as removal of riparian vegetation or N fertilization, may influence the amount of retention attributed to these ecosystem compartments by causing shifts in stoichiometry. Our analysis suggests that C:N of ecosystem compartments can be used to link N-cycling models across streams.

Donnelly, J., D. G. Stickney, et al. (1993). "PROXIMATE AND ELEMENTAL COMPOSITION AND ENERGY CONTENT OF MESOPELAGIC CRUSTACEANS FROM THE EASTERN GULF OF MEXICO." *Marine Biology* **115**(3): 469-480.

The proximate and elemental chemical compositions of 25 species of pelagic decapod and mysid crustaceans collected from the eastern Gulf of Mexico (approximately 27-degrees-N; 86-degrees-W, 1984 to 1989) was examined. Water level ranged from 63 to 95% and increased slightly with species' increased depth of occurrence. Protein levels were generally high (1.5 to 18.3% wet wt,

WW; 27.6 to 62.4% ash-free dry wt, AFDW) and comprised the primary organic component in the majority of species. Protein, both as % WW and % AFDW, decreased with increased depth of occurrence. In contrast to protein, lipid levels were low (0.5 to 8.9% WW; 5.7 to 60.9% AFDW), and increased with increased depth of occurrence. Carbon and nitrogen best mirrored measured lipid and protein levels when considered as non-protein carbon and non-chitin nitrogen, respectively. C:N ratios increased with increased depth, consistent with changes in protein and lipid with depth. Because of their compositional attributes, resident Gulf of Mexico species have a low total wet weight energy content relative to species from more productive regions. Energy content showed no significant trend with depth. Vertical migration patterns were distinctly different between shallow- and deep-living gulf species and these differences were largely responsible for the relationships observed between composition and depth. In migrating species, the protein and nitrogen content were higher, the lipid and carbon contents and C:N ratio lower, than in non-migrating species. Three deep-living species of the genus *Acanthephyra* were found to be compositionally atypical, resembling shallow, migrating types rather than other deep-living, non-migratory species.

Donner, S. D. (2007). "Surf or turf: A shift from feed to food cultivation could reduce nutrient flux to the Gulf of Mexico." Global Environmental Change-Human and Policy Dimensions **17**(1): 105-113.

The extensive use of nitrogen fertilizer on the central U.S. croplands contributes to nitrogen loading by the Mississippi River and the development of seasonal hypoxia in the Gulf of Mexico. The majority of grains cultivated on central U.S. croplands are used as animal feed, rather than directly as human food. In this study, the IBIS-THMB nitrogen modeling system is used to demonstrate how a shift away from meat production from Mississippi Basin crops could reduce total land and fertilizer demands by over 50%, without any change in total production of human food protein. The change would return nitrate-nitrogen export by the Mississippi River to levels at which the Gulf of Mexico "dead zone" has been small or non-existent. An analysis of future land use scenarios and other mitigation proposals, including the construction of riparian wetlands, indicates that a reduced focus on beef production may need to be a part of nitrogen management policy in the Mississippi Basin. (c) 2006 Elsevier Ltd. All rights reserved.

Donner, S. D., M. T. Coe, et al. (2002). "Modeling the impact of hydrological changes on nitrate transport in the Mississippi River Basin from 1955 to 1994." Global Biogeochemical Cycles **16**(3).

[1] The export of nitrate by the Mississippi River to the Gulf of Mexico has tripled since the 1950s primarily due to an increase in agricultural fertilizer application and hydrological changes. Here we have adapted two physically based models, the Integrated Biosphere Simulator (IBIS) terrestrial ecosystem model and the Hydrological Routing Algorithm (HYDRA) hydrological transport model, to simulate the nitrate export in the Mississippi River system and isolate the role of

hydrological processes in the observed increase and interannual variability in nitrate export. Using an empirical nitrate input algorithm based on constant land cover and variability in runoff, the modeling system is able to represent much of the spatial and interannual variability in aquatic nitrate export. The results indicate that about a quarter of the sharp increase in nitrate export from 1966 to 1994 was due to an increase in runoff across the basin. This illustrates the pivotal role of hydrology and climate in the balance between storage of nitrate in the terrestrial system and leaching.

Donner, S. D., C. J. Kucharik, et al. (2004). "Impact of changing land use practices on nitrate export by the Mississippi River." Global Biogeochemical Cycles **18**(1).

[1] The increased use of nitrogen fertilizer in the Mississippi River Basin since the 1950s has been blamed for declining water quality, the degradation of aquatic ecosystems and the growth of a seasonal hypoxic zone in the Gulf of Mexico. In this study, we use the IBIS terrestrial ecosystem model and the HYDRA aquatic transport model to examine how agricultural practices and climate influenced terrestrial and aquatic nitrogen cycling across the Mississippi Basin and the nitrate export to the Gulf. The modeling system accurately depicts the observed trends and interannual variability in nitrate export by the Mississippi River ($r^2 > 0.83$), and several of the major tributaries, between 1960 and 1994. The challenge of simulating nitrate export from the central western sub-basins highlights the key role of processes like denitrification. The simulations demonstrate that three factors led to the doubling of nitrate export by the Mississippi River since 1960: (1) an increase in fertilizer application rates, particularly on maize; (2) an increase in runoff across the basin; and (3) the expansion of soybean cultivation. By the early 1990s, fertilized crops may have accounted for almost 90% of the nitrate leached to the river system, despite representing only 20% of the watershed area. The majority of the nitrate exported to the Gulf appears to originate from "hot spots," including a stretch of the "Corn Belt" across Iowa, Illinois, and Indiana. The relative contribution of such heavily fertilized lands, particularly those in close proximity to higher order streams, can be even greater during wet years.

Dortch, Q. and T. E. Whitledge (1992). "DOES NITROGEN OR SILICON LIMIT PHYTOPLANKTON PRODUCTION IN THE MISSISSIPPI RIVER PLUME AND NEARBY REGIONS." Continental Shelf Research **12**(11): 1293-1309.

The Mississippi River carries very high concentrations of nutrients into the otherwise oligotrophic Gulf of Mexico, resulting in high primary production and hypoxia along the Louisiana continental shelf. The hypothesis that nitrogen availability controls and ultimately limits phytoplankton production on the shelf was tested by measuring an indicator of nitrogen deficiency, the ratio of intracellular free amino acids/particulate protein (AA/Pr), in the area of the Mississippi River plume on a spring and a summer cruise. Neither AA/Pr ratios or nutrients in the water showed nitrogen limitation to be widespread. Ammonium concentrations were generally quite high, so the lack of phytoplankton nitrogen deficiency can be explained by rapid regeneration rates. Nitrogen limitation was

most likely in the summer at high salinities. However, ratios of dissolved nutrient concentrations suggested that silicate was as likely, or sometimes more likely, to be a limiting nutrient than nitrogen. Although silicate depletion may not cause a decrease in productivity, it could result in major changes in phytoplankton size and species composition, and ultimately influence trophodynamics, regeneration, the fate of carbon, and severity and extent of hypoxia.

Duan, S. and T. S. Bianchi (2007). "Particulate and dissolved amino acids in the lower Mississippi and Pearl Rivers (USA)." Marine Chemistry **107**(2): 214-229.

In this study, we present seasonal changes (monthly samples from September 2001 to August 2003) in the abundance and composition of dissolved and particulate amino acids, at one station in the lower Mississippi and Pearl Rivers (LA, MS: USA). Spatial changes over a 4-day transit from river km 390 to river mouth (Head of Passes, LA) in the Mississippi River, and a two-day downstream sampling from Jackson (MS) to Stennis Space Center (MS) were also determined. Temporal data in the lower Mississippi River showed significantly lower concentrations of dissolved combined amino acids (DCAA, 0.8 to 2.2 μM) and dissolved amino acids in high molecular weight fraction (HMW DAA, 0.2-0.4 μM) than in the Pearl River (DCAA, 1.4-4.3 μM ; HMW DAA, 0.4-1.4 μM). Dissolved free amino acids (DFAA) were significantly lower than DCAA in both rivers, and displayed minimal seasonal variability. DCAA, HMW DAA, and particulate amino acids (PAA) were generally higher during high-flow periods, which may have suggested dominance in terrestrial sources. Carbon-normalized yield of PAA (%C-PAA) was generally higher during low-flow conditions and positively correlated with chlorophyll-a (chl-a), reflective of in situ sources. Downstream variability in the lower Mississippi River showed stable DCAA concentrations, a decline in PAA (from 1.06 to 0.43 μM), and a gradual increase in mole percent of non-protein amino acids (%NPAA). This likely reflected bacterial degradation of phytoplankton biomass during falling discharge. Nitrogen-normalized yield of PAA (%N-PAA) was inversely correlated with PAA ($R = -0.7$, $n = 48$), indicative of short-term sedimentation and resuspension events. Conversely, downstream decreases in DCAA and middle-reach peaks of PAA and % N-PAA in the Pearl River, likely resulted from photochemical degradation of DOM as well as algal production during base-flow conditions. The comparisons in abundance and composition of DAA and PAA in these different river systems provides important information on in situ nitrogen and carbon cycling as related to riverine inputs of organic matter to coastal ocean. (c) 2007 Elsevier B.V. All rights reserved.

Duan, S. W. and T. S. Bianchi (2006). "Seasonal changes in the abundance and composition of plant pigments in particulate organic carbon in the lower Mississippi and Pearl Rivers." Estuaries and Coasts **29**(3): 427-442.

Plant pigments in particulate organic carbon were examined in the lower Mississippi and Pearl Rivers (U.S.), along with physical variables and nutrients to study seasonal changes in the abundance and composition of phytoplankton. Water samples were collected monthly from September 2001 to August 2003 in

the lower Mississippi River (MR; no samples were taken in February 2002) and from August 2001 to July 2003 in the Pearl River (PR). High concentrations of total suspended solids (TSS), nutrients, and chlorophyll a (chl a; dominated by diatoms) were observed in the lower MR. The smaller blackwater PR was characterized by lower nutrients and chl a, higher ultraviolet absorbance, and a phytoplankton biomass dominated by chlorophytes. Chl a concentrations in the lower MR was high in summer low-flow periods and also during interims of winter and spring, and did not couple with physical variables and nutrients, likely due to a combination of in situ production and inputs from reservoirs, navigation locks, and oxbow lakes in the upper MR and Missouri River. Chl a concentrations in the PR was only high in summer low-flow periods and were controlled by temperature and concentrations of chromophoric dissolved organic matter (CDOM). The high, diatom-dominated phytoplankton biomass in the lower MR was likely the result of decreasing TSS (increased damming in the watershed) and increasing nutrients (enhanced agricultural runoff) over the past few decades. Lower phytoplankton biomass (dominated by chlorophytes) in the PR was likely linked with intense shading by CDOM and lower availability of nutrient inputs. An increase in the relative importance of phytoplankton biomass in large turbid rivers, such as the MR, could have significant effects on the age and lability of riverine organic matter entering the ocean, the stoichiometric balance of nutrients delivered to coastal margins, and the sequestration of atmospheric CO₂ in these dynamic regions.

Duan, S. W., T. S. Bianchi, et al. (2007). "Temporal variability in the composition and abundance of terrestrially-derived dissolved organic matter in the lower Mississippi and Pearl Rivers." Marine Chemistry **103**(1-2): 172-184.

Here we report on temporal changes in the concentration and composition of lignin phenols in high molecular weight ($< 0.2 \mu\text{m}$, $> 1 \text{ kDa}$) dissolved organic matter (HMW DOM) collected from the lower Mississippi and Pearl Rivers (MR and PR) (USA). Monthly water samples were collected at a station in the lower reach in each river from August 2001 to August 2003. Significantly higher concentrations of lignin and As values (mg lignin phenols in 100 mg organic carbon) in the Pearl River than in the Mississippi River, reflected sporadic inputs of terrestrial DOM during rainstorm events from wetlands and forest soils. Larger seasonal variations in lignin concentration and composition in the Pearl River, compared to the Mississippi River, were attributed to shifts in organic matter sources from topsoil inputs during rainstorm events to groundwater inputs and in situ production during base flow in this small river. Conversely, lower Lambda(8) and vanillic acid to vanillin ratios [(Ad/Al)v] in the HMW DOM of the lower Mississippi River may be a result of a lower export rate of lignin from agricultural soils due to lower carbon storage in the expansive agricultural systems of the Mississippi River watershed, as well as dilution of phytoplankton DOM inputs. Large seasonal changes in lignin concentration and As (linked at times with river discharge), and minimal variability in the composition of lignin phenols, likely represented an integrated signal of soil-derived vascular inputs from the upstream drainage basin. If we are to better understand the controls of organic

matter delivery to the coastal zone from both small and large rivers, sampling strategies need to be adjusted to account for the different scales of hydrologic response time and in situ processing associated with different residence times. (c) 2006 Elsevier B.V All rights reserved.

Escobar, E., M. Lopez, et al. (1997). "Density and biomass of the meiofauna of the upper continental slope in two regions of the Gulf of Mexico." Ciencias Marinas **23**(4): 463-489.

A comparative study of the density and biomass of the meiofauna distributed on the upper continental slope of the western and southern Gulf of Mexico was conducted on board the R/V Justo Sierra. A total of 48 samples were obtained with the aid of a Gomex box corer, at depths ranging from 196 to 540 m off the coast of Tamaulipas and Yucatan. Both regions have contrasting hydrographic and sedimentary conditions; the former is of terrigenous nature, while the latter is carbonaceous. The highest density and biomass values (mean = 1,829,216 +/- 489,005 ind/m²) and 0.304 +/- 0.082 gC/m², respectively) were recorded off Tamaulipas. These parameters were five to six times lower in order of magnitude in the Yucatan slope. Meiofauna biomass values were significantly correlated with density ($r^2 = 0.99$). Significant differences in density [$F_c(1,46) = 38.51$, $P < 0.005$] and biomass [$F_c(1,46) = 37.72$, $P < 0.005$] were recognized between both areas studied. No clear spatial or bathymetric patterns were observed in the meiofaunal components identified in Tamaulipas. This pattern was attributed to the prevailing variable hydrographic conditions and the different organic carbon sources present in the western region of the Gulf of Mexico. In contrast, the depth and particulate organic carbon of the Yucatan slope exert a significant influence on meiofaunal density and biomass. In this region, predation by larger size classes seems to control the density. The density and biomass values recorded in both regions of the gulf studied fall within the range of previous meiofauna reports from the northern Gulf of Mexico and similar slope habitats of the world oceans.

EscobarBriones, E. G. and L. A. Soto (1997). "Continental shelf benthic biomass in the western Gulf of Mexico." Continental Shelf Research **17**(6): 585-604.

Benthic biomass of the soft-bottom community of the continental shelf in the western Gulf of Mexico reveals a significant space and time variability according to data obtained in three cruises during 1988 and 1989. This system is highly influenced by the hydrographic regime defined by anticyclonic ring interactions, convective mixing, and river runoff and fronts. Total benthic biomass varied among cruises and spatially by almost three orders of magnitude. High values (2.01-1.22 g C.m⁻²) were found in April 1989 and September 1988 (stratified period), and low values (0.33 g C.m⁻²) were found in November 1989 (mixed period). The northerly winter wind stress promotes coupling between pelagic and benthic compartments with the refurbishing of the benthic community with surface water carbon food sources. Small scale variability, due to either hydrological or sedimentological factors, accounts for the patchy distribution observed and large standard deviation recorded. Shelf benthic biomass was

inversely related to depth: total benthos ($r^2 = 0.70$), epibenthic macrofauna ($r^2 = 0.82$), and infauna ($r^2 = 0.71$). Largest total biomass values were obtained in areas influenced by river runoff and showed a northward increase in biomass during the stratified condition and southward in the period of mixing. These trends were likely related to wind transport of organic matter from riverine sources or production stimulated by riverine nutrient fluxes. Biomass values reported here are similar to others from similar depths in the Gulf of Mexico and worldwide. (C) 1997 Elsevier Science Ltd.

Fahnenstiel, G. L., M. J. McCormick, et al. (1995). "TAXON-SPECIFIC GROWTH AND LOSS RATES FOR DOMINANT PHYTOPLANKTON POPULATIONS FROM THE NORTHERN GULF-OF-MEXICO." Marine Ecology-Progress Series **117**(1-3): 229-239.

Taxon-specific growth and sedimentation rates of dominant phytoplankton were measured during 2 cruises (summer 1990 and spring 1991) in the northern Gulf of Mexico as part of the NOAA Nutrient-Enhanced Coastal Ocean Productivity (NECOP) program. Microzooplankton grazing rates also were measured during the summer cruise. During each of the cruises, a series of stations from the Mississippi River mouth to the hypoxia region (located ca 50 to 100 km west) were sampled to examine variability of growth and loss processes along a strong environmental gradient. Significant taxa- and group-specific differences were noted for both growth and loss rates. Growth rates ranged from <0.1 to 3.0 d^{-1} with highest rates in the plume region during the summer cruise, where surface rates were close to or exceeded previous $\mu(\text{max})$, values for several taxa. For all taxa, growth rates were lower in the hypoxia region (mean = 0.5 d^{-1}) than in the plume region (mean = 1.1 d^{-1}); soluble nitrogen concentrations explained over 50 % of the variability in growth rates. Diatom growth rates were similar to non-diatoms in the plume region, but were significantly lower in the hypoxia region, which suggests that silica limitation may exist in this region. The fate of phytoplankton appeared to be controlled by size and by the degree of silicification. Significant microzooplankton grazing loss rates were noted only for small taxa ($<20 \mu\text{m}$). For microflagellates, microzooplankton grazing rates averaged 82 % (range 42 to 214%) of the growth rate; sedimentation rates were always $<1\%$ of the growth rate. Sedimentation was an important loss for several diatoms, with significant taxon-specific and seasonal differences noted. Large colonial diatoms, such as *Skeletonema costatum* and *Thalassiosira rotula*, exhibited the highest sedimentation rates in the plume region during the spring cruise (0.2 to 1.0 d^{-1}), whereas the lowest rates ($< 0.01 \text{ d}^{-1}$) were noted for *Rhizosolenia fragilissima* and *Ceratium tulina pelagica* in the hypoxia region during the summer cruise. Our results suggest that in the northern Gulf of Mexico, phytoplankton rate processes proceed very rapidly, with growth rates primarily controlled by the supply of nitrogen via the Mississippi River and the fate controlled primarily by size and density (silicification).

Fang, J. S., T. A. Abrajano, et al. (1993). "GULF-OF-MEXICO HYDROCARBON SEEP COMMUNITIES .11. CARBON ISOTOPIC FRACTIONATION DURING FATTY-ACID BIOSYNTHESIS OF SEEP ORGANISMS AND ITS IMPLICATION FOR

CHEMOSYNTHETIC PROCESSES." Chemical Geology **109**(1-4): 271-279.

The individual fatty acids of mytilids and vestimentiferan (*Escarpiis* sp.) from hydrocarbon seeps exhibit light $\delta^{13}\text{C}$ -values: from -56.9 to -49.0 parts per thousand for the mytilids and from -38.6 to -31.6 parts per thousand for the vestimentiferan. Unsaturated fatty acids have lighter $\delta^{13}\text{C}$ than saturated ones. The variations in $\delta^{13}\text{C}$ are up to 5.1-6.7 parts per thousand (mytilids) and 7.0 parts per thousand (vestimentiferan) within a single specimen. It is suggested that a kinetic isotopic effect in the biosynthesis of fatty acids and intermolecular isotope fractionation during fatty acid desaturation and elongation are responsible for the observed distribution pattern. Fatty acids are depleted in C-13 relative to the gills of the mytilids, whereas fatty acids of the vestimentiferan are enriched relative to trophosomes. The difference in $\delta^{13}\text{C}$ of fatty acids between mytilids and vestimentiferan reflects the differences in substrates (methane vs. CO_2), and the different chemosynthetic processes of the invertebrates.

Filipek, L. H. and R. M. Owen (1980). "EARLY DIAGENESIS OF ORGANIC-CARBON AND SULFUR IN OUTER SHELF SEDIMENTS FROM THE GULF-OF-MEXICO." American Journal of Science **280**(10): 1097-1112.

Fisher, C. R., J. M. Brooks, et al. (1993). "THE COOCCURRENCE OF METHANOTROPHIC AND CHEMOAUTOTROPHIC SULFUR-OXIDIZING BACTERIAL SYMBIONTS IN A DEEP-SEA MUSSEL." Marine Ecology-Pubblicazioni Della Stazione Zoologica Di Napoli I **14**(4): 277-289.

In April 1990 a new species of mytilid containing bacterial endosymbionts was discovered at a deep-water seep site within Alaminos Canyon in the Gulf of Mexico. Activities of ribulose biphosphate carboxylase/oxygenase and ATP sulfurylase, as well as the presence of substantial levels of elemental sulfur in the gill tissues indicate the presence of chemoautotrophic sulfuroxidizing symbionts in the gills. Methanol dehydrogenase activity and the tissue stable carbon isotope ratios indicate the presence of methanotrophic bacteria in the gills of the same animals. Two distinct size classes and morphological types of gram negative bacteria are visible in transmission electron micrographs of the gill tissue, one of which contains the complex internal membranes typical of methanotrophs. Both general types of symbionts have been demonstrated singly in related species of deep-sea mytilids. In this species, however, both types are found in single individuals, often within the same cell vacuole.

Fisher, C. R. and J. J. Childress (1992). "ORGANIC-CARBON TRANSFER FROM METHANOTROPHIC SYMBIONTS TO THE HOST HYDROCARBON-SEEP MUSSEL." Symbiosis **12**(3): 221-235.

The mechanism of transfer of fixed carbon from methanotrophic symbionts to their host (an undescribed mussel found in association with hydrocarbon seeps in the Gulf of Mexico) was investigated through ultrastructural observations and incubations with C-14 -methane. Unlike other autotrophic symbioses studied with labeled inorganic carbon, there was no appreciable transfer of labeled organic

carbon from the symbiont-containing tissues to symbiont-free tissues during a 2 hour pulse and two hour chase period. However, after 1 and 5-day chase periods, quantitative transfer of labeled organic carbon into symbiont-free tissues was documented. We propose that the longer time course of transfer of label in this association is due to host digestion of symbionts, rather than translocation of small molecular weight compounds from symbiont to host. Additional evidence for this was found in the presence of abundant secondary lysosomes in the host bacteriocytes, which often contain easily recognized remnants of the symbionts.

Formolo, M. J., T. W. Lyons, et al. (2004). "Quantifying carbon sources in the formation of authigenic carbonates at gas hydrate sites in the Gulf of Mexico." Chemical Geology **205**(3-4): 253-264.

The northern slope of the Gulf of Mexico is known for extensive venting of methane and other hydrocarbons as related to active salt diapirism and associated fault conduits which link world-class subsurface reserves to seafloor seeps. These venting hydrocarbons fuel extensive micro- and macrofaunal cold seep communities. Of particular interest is the relationship between anaerobic methane-oxidizing archaea and sulfate-reducing bacteria. It has been suggested that sulfate-dependent anaerobic methane oxidation dominates carbon oxidation and attendant authigenic carbonate precipitation at these sites. To test this assumption, we have quantified the relative contributions of dissolved carbon dioxide (SigmaCO_2) from a variety of sources—specifically seawater, organic matter, methane, and non-methane liquid and gaseous hydrocarbons—using the carbon isotope compositions of authigenic carbonates and a simple isotopic mass balance. Our model, and a small but representative suite of data from the Gulf, demonstrates that methane is a contributor but is not the dominant source of metabolic energy at the sites of active venting. Instead, oxidation of non-methane hydrocarbons appears to be the primary source of carbonate alkalinity. The secondary role played by methane oxidation has been independently recognized by other workers from organic biomarker relationships and from disparities observed between measured rates of sulfate reduction and methane oxidation. Despite the domination of the carbon reservoir by non-methane sources, oxygen isotope data for the authigenic carbonates bear the mark of appreciable gas hydrate dissociation. This study, rather than being an exhaustive survey of Gulf of Mexico seeps, is intended only to provide a template for the investigation of the abundant authigenic carbonate deposits distributed throughout the geologic record. As in the Gulf of Mexico, many modern and ancient cold seeps are characterized by a complex interplay of carbon sources readily preserved in the $\delta^{13}\text{C}$ values of carbonates. (C) 2004 Elsevier B.V. All rights reserved.

Frederic Ad and W. M. Sackett (1970). "ORGANIC CARBON IN GULF-OF-MEXICO." Journal of Geophysical Research **75**(12): 2199-8.

Fry, B. and S. C. Wainright (1991). "DIATOM SOURCES OF C-13-RICH CARBON IN MARINE FOOD WEBS." Marine Ecology-Progress Series **76**(2): 149-157.

We used stable isotope measurements to investigate the possible nutritional importance of diatoms for consumers in planktonic food webs. Several lines of evidence indicated that rapidly growing diatoms had C-13-rich isotopic compositions in the Georges Bank (USA) ecosystem. Diatoms in spring blooms and in well-mixed summer waters were relatively rich in C-13, with delta-C-13 values in the -15 to -19 parts per thousand range, while other phytoplankton and most particulate organic matter collected over a 13 mo period had C-13-depleted values of -21 to -25 parts per thousand. Culture experiments with nutrient-enriched seawater performed on Georges Bank and in Woods Hole Harbor (MA, USA) also showed a C-13 distinction between fast-growing diatoms with C-13-rich contents and other algae that were depleted in C-13. Zooplankton from central Georges Bank where diatoms are abundant had relatively high delta-C-13 values, consistent with an important nutritional role for C-13 diatoms. We estimate that a minimum of 40% of the carbon present in zooplankton consumers of central Georges Bank is derived from diatoms. Bloom diatoms from the North Atlantic, northeastern Pacific, and the nearshore Gulf of Mexico also had C-13-rich compositions, indicating that diatoms can be a source of C-13-rich carbon in many marine food webs.

Galler, J. J. and M. A. Allison (2008). "Estuarine controls on fine-grained sediment storage in the Lower Mississippi and Atchafalaya Rivers." Geological Society of America Bulletin **120**(3-4): 386-398.

Observations of the lower Mississippi River channel in 1999-2003 with side-scan and subbottom seismic profilers, multibeam bathymetry, core radiotracers (Be-7, (CS)-C-137, Pb-210, and Th-234), and water-column profiles of fluid and suspended sediment properties are utilized to constrain the timing, location, and intensity of the seasonal storage of finegrained sediments in the estuarine channel reach below Venice, Louisiana. Unlike earlier studies that suggested little or no estuarine sedimentation was taking place in the river, the present study demonstrates that the river channel above the Head of Passes seasonally stores as much as 10% of the annual suspended sediment discharge during periods of falling-to-low Mississippi water discharge associated with salt stratification in the channel thalweg. Mud deposits are up to 3.2 m thick with Be-7-derived sediment deposition rates of up to 8.9 mm/day. Water-column profiling and Th-234/Be-7 ratios suggest that (1) particles are transported and settled mainly as flocs; and (2) riverine flocs are settling through the strong salt-wedge halocline and are protected from re-erosion by the salt stratification. With onset of the spring freshet and the corresponding seaward retreat of the saltwater wedge, the entire volume of finegrained material stored in the lower river (except in low freshet years) is remobilized and transported to the Gulf of Mexico in the turbid freshwater plume. This tidal hysteresis strongly influences the timing of sediment supply to the ocean: high turbidities in the shelf plume during rising water discharge spikes of 1- to 2-week duration are the product of local channel floor remobilization as well as increased supply from the drainage basin. Pulsed resupply of sediments and the pore-water products of early diagenesis potentially have major implications for issues such as continental

margin carbon budgets and coastal eutrophication. Companion surveys conducted in the lowermost 12 km reach of the Atchafalaya distributary of the Mississippi show no evidence of saltwater wedge intrusion at low discharge or seasonal fine-grained sediment storage, likely due to the shallow (7 m) river-mouth sill that impedes the upstream movement of Gulf water.

Gardner, W. D., A. Mishonov, et al. (2006). "Global POC concentrations from in-situ and satellite data." Deep-Sea Research Part II-Topical Studies in Oceanography **53**(5-7): 718-740.

During the last three decades significant contributions have been made to understanding regional and global distribution of chlorophyll in the ocean by developing algorithms from ocean-color products. Analogously, in this work empirical algorithms are developed to derive concentrations of particulate organic carbon (POC) from ocean-color products. We combined vertical profiles of particulate beam attenuation coefficient at 660 nm (c_p) collected on numerous cruises during World Ocean Circulation Experiment (WOCE), Joint Global Ocean Flux Study (JGOFS), South Atlantic Ventilation Experiment (SAVE), and other programs since the 1980s to create a global database. Discrete samples of POC and synchronously measured c_p data collected in the Atlantic, Pacific, Indian and Southern oceans during JGOFS and other programs were used to make c_p :POC regressions to convert c_p data to POC values. During the two programs, satellite data were available when synchronous POC samples and c_p profiles were obtained over several seasons. c_p averaged over one attenuation depth in the South Pacific and northeast Gulf of Mexico was correlated with four synchronous ocean-color products. A good correlation was obtained with both normalized water-leaving radiance at 555 nm (LWN(555)) and diffuse attenuation coefficient at 490 nm (K_{490}). Using a combined K_{490} : c_p regression from the two areas, global maps of the estimated mean c_p were created and converted to mean POC concentration down to one attenuation depth for summer and winter seasons. Seasonal $c(p)$, POC and chlorophyll distributions were used to map %CHL and $c(p)$:CHL ratios within one attenuation depth as a possible index of phytoplankton physiology. (c) 2006 Elsevier Ltd. All rights reserved.

Gardner, W. S., R. Benner, et al. (1996). "Effects of high-molecular-weight dissolved organic matter on nitrogen dynamics in the Mississippi River plume." Marine Ecology-Progress Series **133**(1-3): 287-297.

The dynamics of N and its interactions with labile dissolved organic C (DOC), bacteria, and phytoplankton were studied to determine potential effects of dissolved organic matter (DOM) and light on N dynamics in surface waters of the Mississippi River (USA) plume in the Gulf of Mexico. Bacterial uptake of added labeled N compounds ((NH_4^+) -N-15 or N-15-labeled dissolved free amino acids, DFAA) was stimulated more by high-molecular-weight (HMW, >1 kDa) DOM than by low-molecular-weight (LMW, <1 kDa) DOM. An index that inversely indicated the presence of labile DOC was defined as the fraction of assimilated Amino acid-N-15 that was Recovered as N-15-Ammonium (ANRA), following the additions of high-levels (4 μ M) of N-15-DFAA. ANRA ratios were high in the

absence of other available carbon sources because heterotrophic bacteria were forced to use the added amino acids as a carbon source for respiration rather than as a nutrient source for biomass formation. In dynamic light/dark experiments, conducted with in situ populations of organisms, uptake rates of added (NH₄⁺)-N-15 were significantly enhanced both by the presence of light and by the addition of HMW DOM. Uptake rates of added N-15-labeled DFAA were increased by the addition of HMW DOM but not by light. ANRA ratios were consistently lower in the presence of added HMW DOM than in controls. Added HMW DOM thus appeared to stimulate the incorporation of assimilated DFAA into bacterial biomass. Bacterial growth rates were relatively high in both light and dark bottles with DFAA additions and in light bottles with HMW DOM plus NH₄⁺ additions, but they remained comparatively low in dark bottles with added NH₄⁺. These results are consistent with the idea that bacterial N dynamics in these euphotic waters may be tightly coupled to photosynthetic activities over short time scales.

Gardner, W. S., R. Benner, et al. (1994). "MINERALIZATION OF ORGANIC MATERIAL AND BACTERIAL DYNAMICS IN MISSISSIPPI RIVER PLUME WATER." Estuaries 17(4): 816-828.

Net remineralization rates of organic matter and bacterial growth rates were observed in dark-bottle incubation experiments conducted in July-August and February with water samples collected from sites in the Mississippi River plume of the Gulf of Mexico. Our objectives were to measure site-specific degradation rates of labile dissolved and particulate organic matter, quantify the potential importance of bacteria in these processes, and examine the kinetics of degradation over time. Unfiltered samples, and samples treated to remove (or dilute out) particles larger than bacteria, were enclosed in 9-l bottles and incubated in, the dark for 3-5 d. Respiration rates and inorganic compound accumulation rates were higher in summer than in winter and were highest in unfiltered surface samples at sites of intermediate salinities where phytoplankton were most abundant. The ratio of ammonium accumulation to oxygen removal in summer experiments suggested that the mineralized organic material resembled "Redfield" stoichiometry. Chemical fluxes were greater in bottles containing large (>1-3 μm) particles than in the bottles with these particles removed, but bacterial activities were generally similar in both treatments. These results suggest that particle consumers were an important component of total organic matter degradation. However, these experiments may have underestimated natural bacterial degradation rates because the absence of light could affect the production of labile organic substrates by phytoplankton. In agreement, with this hypothesis, bacterial growth rates tended to decrease over time in summer in surface plume waters where phytoplankton were abundant. In conjunction with other data, our results indicate that heterotrophic processes in the water column are spatially and temporally dependent on phytoplankton production.

Gilhooly, W. P., R. S. Carney, et al. (2007). "Relationships between sulfide-oxidizing bacterial mats and their carbon sources in northern Gulf of Mexico cold seeps." Organic

Geochemistry **38**(3): 380-393.

Chemical and isotopic characterization of microbial mats collected from methane and petroleum seeps in the Gulf of Mexico suggest microbial mat color is related to carbon utilization. A survey of white and orange-colored microbial mats collected in the northern Gulf of Mexico from the Brine Pool NR-1 (BP) and a hydrate mound site in Green Canyon 234 (GC 234) during Johnson Sea-Link submersible dives was conducted to explore the bacterial utilization of different carbon sources. Sedimentary organic matter at BP is predominantly derived from biogenic methane whereas organic material available in sediments at GC 234 originates from a mixture of methane and non-methane hydrocarbons. Interstitial sulfide concentrations were significantly elevated in porewater fluids below white mats collected from BP (1.2 +/- 0.2 mM) and below orange mats at GC 234 (6.1 +/- 0.7 mM). Sulfate reduction rates, ranging from 0.4 to 3.8 $\mu\text{mol SO}_4 \text{ cm}^{-1} \text{ d}^{-1}$, indicate rapid sulfate consumption below GC 234 orange mats. A model based on carbon isotopes was used to delineate possible inorganic and organic carbon sources to BP white mats and GC 234 orange mats. The results suggest the white mats are chemoautotrophic and that the orange mats may employ either heterotrophy or autotrophy. (c) 2006 Elsevier Ltd. All rights reserved.

Glasby, G. P. (2003). "Potential impact on climate of the exploitation of methane hydrate deposits offshore." Marine and Petroleum Geology **20**(2): 163-175.

Considerable attention has focussed on methane hydrates as a potential energy resource but much less on the potential environmental problems of exploiting these deposits. In fact, methane hydrate deposits represent a dynamic system formed as a result of the continuous migration of methane gas along fracture systems. Any exploitation of methane hydrates offshore will perforce take place in these unstable systems and could lead to the large-scale release of CH₄ under unfavourable circumstances. However, most of this CH₄ would be oxidized to CO₂ within the water column under steady-state conditions. Only under exceptional circumstances would large-scale release of CH₄ into the atmosphere take place. The impact of exploiting these deposits offshore on global climate may therefore be limited provided serious efforts are made to minimize environmental impacts. At present, prospects for the commercial exploitation of methane hydrates are in their infancy. Considerable ingenuity will be required to satisfy the requirements of safe operating conditions, mitigation of environmental hazards and commercial viability. The need to exercise caution before attempting to exploit these deposits is emphasized. (C) 2003 Published by Elsevier Ltd.

Goni, M. A., E. S. Gordon, et al. (2006). "The effect of Hurricane Lili on the distribution of organic matter along the inner Louisiana shelf (Gulf of Mexico, USA)." Continental Shelf Research **26**(17-18): 2260-2280.

On October 3, 2002 Hurricane Lili made landfall on a previously studied region of the inner Louisiana shelf as a Category 2 storm with winds over 160 km/h. A week after the hurricane, major impacts of the storm were not evident in the water column except for the lower than expected inshore salinities (similar to 12 psu) for this time of year, which was characterized by low river discharge.

Turbidity profiles were typical of those measured during previous investigations with suspended sediment concentrations > 75 mg/L at inshore stations and < 50 mg/L in surface waters And offshore. The implication is that the sediments resuspended during the hurricane settled soon after the storm passage. Water column particulate organic carbon (POC) concentrations ranged from 0.1 to over 2.0 mg/L, with the highest concentrations measured near the seabed and in the inshore portions of the study area. Suspended particles were characterized by low organic matter content (%POC of 0.5-2 wt%), low chlorophyll:POC ratios (Chl:POC < 4 mg/g) and moderately elevated POC:particulate nitrogen ratios (POC:PN of 10-14mol/mol), all suggesting their source was locally resuspended seabed sediment rather than from algal biomass or land-derived vascular plant detritus. Post hurricane sediment deposition throughout the study area resulted in a storm layer that ranged from < 0.5 to 20 cm in thickness. In most locations sediment accumulation ranged from 3 to 10cm. The storm deposits were generally composed of silty clays with a coarser, somewhat sandy 1-2cm basal layer. Surface sediments from the storm layer were characterized by relatively high mineral surface areas (SA of 30-50m²/g) and elevated OC contents (%OC of 1.0-2.0%). The dispersal of fine sediments following the hurricane resulted in marked changes in the SA and %OC values of surface sediments from offshore locations, which prior to the storm contained coarser, organic-poor particles (SA of 5-15 m²/g and %OC of 0.2-0.6%). The OC:SA and OC:N ratios of storm layer sediments ranged from 0.4 to 0.6 mg OC/m² and from 10 to 12 mol/mol, respectively, and were comparable to those measured in surface sediments prior to the hurricane. Such similarities in the composition of the organic matter reinforce the idea that the source of the storm deposits was the finer fraction of resuspended seabed sediments, with little evidence for inputs from local land-derived sources or autochthonous algal production. Overall, the magnitude of sediment and organic matter deposition on the seabed after the storm greatly exceeded the annual inputs from the Atchafalaya River and coastal primary production. The combined effects of hurricane-driven erosion and post-storm deposition represent a major perturbation to the benthic community of the region, which is already subject to these types of disturbances due to the combined effects of peaks in river discharge and the passage of storm fronts. (c) 2006 Elsevier Ltd. All rights reserved.

Goni, M. A., N. Monacci, et al. (2006). "Distribution and sources of particulate organic matter in the water column and sediments of the Fly River Delta, Gulf of Papua (Papua New Guinea)." Estuarine Coastal and Shelf Science **69**(1-2): 225-245.

Suspended particles from surface and bottom waters and surficial sediments from the seabed were collected throughout the Fly River sub-aqueous delta region during the monsoon season in January 2003. Because of the unusually low river discharge associated with a strong El Nino, water-column salinities were relatively high (10 to 32) throughout most of the delta, with brackish salinities (< 10) only measured within the main distributary channel of the Fly River. The concentration and composition of particulate organic matter (POM) in these samples showed distinct spatial differences and marked contrasts between water

column and seabed samples. Overall, relatively low concentrations of total suspended solids (TSS), particulate organic carbon (POC) and particulate nitrogen (PN) were measured in surface (27 +/- 50, 0.83 +/- 1.2, and 0.05 +/- 0.05 mg/L, respectively) and bottom (400 +/- 743, 7.1 +/- 7.3, and 1.7 +/- 7.2 mg/L, respectively) waters throughout the delta. Particles in both surface and bottom waters displayed elevated organic carbon contents (%OC > 4 wt.%), relatively high organic carbon:nitrogen molar ratios (OC:N > 20 mol:mol) and quite depleted stable isotopic compositions of organic carbon (delta C-13(OC) < -27 parts per thousand). In contrast, surface sediments in the seabed displayed spatially uniform compositions that were characterized by markedly lower %OC contents (1.1 +/- 0.8 wt.%), lower OC:N ratios (17.9 mol:mol) and relatively enriched delta C-13(OC) compositions (-25.5 +/- 1.1‰). The radioisotopic compositions of OC from a selected set of seabed samples (Delta C-14(OC) of -408 +/- 82‰) indicate OM in surface sediments is old (C-14 ages of 2800 to over 6000 years before present). The ratios of organic carbon to mineral surface area exhibited by these sediments are within the typical (mono-layer equivalent) ranges characteristic of shelf sediments and do not reflect the preferential removal of terrigenous OM. Overall, these compositions indicate that while water-column POM appears to be derived mainly from terrigenous vascular plant debris and riverine/estuarine phytoplankton, the source of most of the sedimentary POM is aged, soil OC ultimately derived from C3 vegetation. We speculate that the concentrations and sources of suspended POM in the water column of the Fly River delta region reflect the conditions of low river discharge, low wave energy and neap tides encountered at the time of sampling. In contrast, POM compositions in surface sediments are consistent with the transport and deposition of old, mineral-bound OC most likely eroded from the upland regions of the Fly River watershed, which is characterized by steep slopes, high precipitation and C3 tropical forests and grasslands. (c) 2006 Elsevier Ltd. All rights reserved.

Goni, M. A., K. C. Ruttenberg, et al. (1997). "Source and contribution of terrigenous organic carbon to surface sediments in the Gulf of Mexico." *Nature* **389**(6648): 275-278.

The sources and burial processes of organic matter in marine sediments are not well understood, yet they are important if we are to have a better understanding of the global carbon cycle(1). In particular, the nature and fraction of the terrestrial organic carbon preserved in marine sediments is poorly constrained. Here we use the chemical and stable carbon isotope signatures of oxidation products from a macromolecular component (lignin)(2) of the terrigenous organic matter preserved in offshore surface sediments in the Gulf of Mexico to complement similar data from an existing onshore transect(3) in this region. The complete onshore-offshore data set, along with radiocarbon dates of the bulk organic material at the same sites, allows the differentiation of material originating from plants that photosynthesize using the C-4 mechanism from those that undergo C-3 photosynthesis. We conclude that the offshore lignins derive from erosion of the extensive grassland (C-4) soils of the Mississippi River drainage basin, and that the nearshore lignins originate largely from C-3 plant

detritus from coastal forests and swamps, This distribution is probably due to the hydrodynamic sorting of the different source materials(4) during their seaward transport, These results suggest that previous studies(3,5) have significantly underestimated the terrigenous fraction of organic matter in offshore sediments by not recognizing the contribution of C-4 vegetation to the carbon-isotope composition. Such an underestimate may force revisions in the assessment of past marine primary productivity and associated organic carbon fluxes(6), and of organic matter preservation/remineralization(7) and nutrient cycling(8) in marine sediments.

Goni, M. A., K. C. Ruttenberg, et al. (1998). "A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico." Geochimica Et Cosmochimica Acta **62**(18): 3055-3075.

Organic matter in surface sediments from two onshore-offshore transects in the northwestern Gulf of Mexico was characterized by a variety of techniques, including elemental, stable carbon, radiocarbon, and molecular-level analyses. In spite of the importance of the Mississippi River as a sediment source, there is little evidence for a significant terrigenous input based on the low carbon:nitrogen ratios (8-5) and the enriched $\delta^{13}\text{C}$ values of bulk sedimentary organic carbon (-19.7 parts per thousand to -21.7 parts per thousand). Radiocarbon analyses, on the other hand, yield depleted $\Delta^{14}\text{C}$ values (-277 parts per thousand to -572 parts per thousand) which indicate that a significant fraction of the sedimentary organic carbon (OC) in all these surface sediments must be relatively old and most likely of allochthonous origin. CuO oxidations yield relatively low quantities of lignin products (0.4-1.4 mg/100 mg OC) along with compounds derived from proteins, polysaccharides, and lipids. Syringyl:vanillyl and cinnamyl:vanillyl ratios (averaging 1.6 and 0.5, respectively) and acid:aldehyde ratios for both vanillyl and syringyl phenols (averaging 0.8 and 1.2, respectively) indicate that the lignin present in sediments originates from nonwoody angiosperm sources and is highly degraded. The $\delta^{13}\text{C}$ values of lignin phenols in shelf sediments are relatively depleted in C-13 (averaging -26.3 parts per thousand) but are increasingly enriched in C-13 at the slope sites (averaging -17.5 parts per thousand for the two deepest stations). We interpret these molecular and isotopic compositions to indicate that a significant fraction (greater than or equal to 50%) of the lignin and, by inference, the land-derived organic carbon in northwestern Gulf of Mexico sediments ultimately originated from C-4 plants. The source of this material is likely to be soil organic matter eroded from the extensive grasslands of the Mississippi River drainage basin. Notably, the mixed C-4 and C-3 source and the highly degraded state of this material hampers its recognition and quantification in shelf and slope sediments. Our data are consistent with higher than previously estimated inputs of land-derived organic carbon to regions of the ocean, such as the Gulf of Mexico, with significant sources of terrigenous C-4-derived organic matter. Copyright (C) 1998 Elsevier Science Ltd.

Goni, M. A., M. J. Teixeira, et al. (2003). "Sources and distribution of organic matter in a

river-dominated estuary (Winyah Bay, SC, USA)." Estuarine Coastal and Shelf Science **57**(5-6): 1023-1048.

The sources and distribution of organic matter (OM) in surface waters and sediments from Winyah Bay (South Carolina, USA) were investigated using a variety of analytical techniques, including elemental, stable isotope and organic biomarker analyses. Several locations along the estuary salinity gradient were sampled during four different periods of contrasting river discharge and tidal range. The dissolved organic carbon (DOC) concentrations of surface waters ranged from 7 mg l⁻¹ in the lower bay stations closest to the ocean to 20 mg l⁻¹ in the river and upper bay samples. There was a general linear relationship between DOC concentrations and salinity in three of the four sampling periods. In contrast, particulate organic carbon (POC) concentrations were significantly lower (0.1-3 mg l⁻¹) and showed no relationship with salinity. The high molecular weight dissolved OM (HMW DOM) isolated from selected water samples collected along the bay displayed atomic carbon: nitrogen ratios ([C/N]_a) and stable carbon isotopic compositions of organic carbon (delta(13)C(OC)) that ranged from 10 to 30 and from -28 to -25 parts per thousand, respectively. Combined, such compositions indicate that in most HMW DOM samples, the majority of the OM originates from terrigenous sources, with smaller contributions from riverine and estuarine phytoplankton. In contrast, the [C/N]_a ratios of particulate OM (POM) samples varied significantly among the collection periods, ranging from low values of similar to 5 to high values of >20. Overall, the trends in [C/N]_a ratios indicated that algal sources of POM were most important during the early and late summer, whereas terrigenous sources dominated in the winter and early spring. In Winyah Bay bottom sediments, the concentrations of the mineral-associated OM were positively correlated with sediment surface area. The [C/N]_a ratios and delta(13)C(OC) compositions of the bulk sedimentary OM ranged from 5 to 45 and from -28 to -23 parts per thousand, respectively. These compositions were consistent with predominant contributions of terrigenous sources and lesser (but significant) inputs of freshwater, estuarine and marine phytoplankton. The highest terrigenous contents were found in sediments from the river and upper bay sites, with smaller contributions to the lower parts of the estuary. The yields of lignin-derived CuO oxidation products from Winyah Bay sediments indicated that the terrigenous OM in these samples was composed of variable mixtures of relatively fresh vascular plant detritus and moderately altered soil OM. Based on the lignin phenol compositions, most of this material appeared to be derived from angiosperm and gymnosperm vascular plant sources similar to those found in the upland coastal forests in this region. A few samples displayed lignin compositions that suggested a more significant contribution from marsh C-3 grasses. However, there was no evidence of inputs of *Spartina alterniflora* (a C-4 grass) remains from the salt marshes that surround the lower sections of Winyah Bay. (C) 2003 Elsevier Ltd. All rights reserved.

Goni, M. A. and K. A. Thomas (2000). "Sources and transformations of organic matter in surface soils and sediments from a tidal estuary (north inlet, South Carolina, USA)." Estuaries **23**(4): 548-564.

Surface soil and sediment samples collected along a forest-brackish marsh-salt marsh transect in a southeastern U.S. estuary were separated into three different fractions (sand, macro-organic matter, and humus) based on size and density. Elemental, stable carbon isotope, and lignin analyses of these samples reveal important contrasts in the quantity, composition, and sources of organic matter between Forest and marsh sites. Elevated nitrogen contents in humus samples suggest nitrogen incorporation during humification is most extensive in forest soils relative to the marsh sites. The lignin compositions of the macro-organic and humus samples reflect the predominant type of vegetation at each site. Lignin phenol ratios indicate that woody and nonwoody litter from gymnosperm and angiosperm trees (pines and oaks) is the major source of vascular plant-derived organic matter in the forest site and that angiosperm grasses (*Juncus* and *Spartina*) are the major sources of lignin at the marsh sites. The phenol distributions also reveal that oxidative degradation of Lignin is most extensive in the forest and brackish marsh zones whereas little Lignin decay occurs in the salt marsh samples. In forest soils, most organic matter originates from highly altered forest vegetation while at the brackish marsh site organic matter is a mixture of degraded *Juncus* materials and microbial/algal remains. Organic matter in the salt marsh appears to be composed of a more complex mixture of sources, including degraded *Spartina* detritus as well as algal and microbial inputs. Microbial methane oxidation appears to be an important process and a source of C-15 depleted organic carbon in subsurface sediments at this site.

Gordon, E. S. and M. A. Goni (2003). "Sources and distribution of terrigenous organic matter delivered by the Atchafalaya River to sediments in the northern Gulf of Mexico." *Geochimica Et Cosmochimica Acta* **67**(13): 2359-2375.

Suspended sediments (SS) from the Atchafalaya River (AR) and the Mississippi River and surficial sediment samples from seven shallow cross-shelf transects west of the AR in the northern Gulf of Mexico were examined using elemental (%OC, C/N), isotopic ($\delta^{13}\text{C}$, $\Delta^{14}\text{C}$), and terrigenous biomarker analyses. The organic matter (OM) delivered by the AR is isotopically enriched (similar to -24.5‰) and relatively degraded, suggesting that soil-derived OM with a C₄ signature is the predominant OM source for these SS. The shelf sediments display OC values that generally decrease seaward within each transect and westward, parallel to the coastline. A strong terrigenous C/N (29) signal is observed in sediments deposited close to the mouth of the river, but values along the remainder of the shelf fall within a narrow range (8-13), with no apparent offshore trends. Depleted stable carbon isotope ($\delta^{13}\text{C}$) values typical of C₃ plant debris (-27‰) are found near the river mouth and become more enriched (-22 to -21‰) offshore. The spatial distribution of lignin in shelf sediments mirrors that of OC, with high lignin yields found inshore relative to that found offshore (water depth > 10 m). The isotopic and biomarker data indicate that at least two types of terrigenous OM are deposited within the study area. Relatively undegraded, C₃ plant debris is deposited close to the mouth of the AR, whereas more degraded, isotopically enriched, soil-derived OM

appears to be deposited along the remainder of the shelf. An important input from marine carbon is found at the stations offshore from the 10-m isobath. Quantification of the terrigenous component of sedimentary OM is complicated by the heterogeneous composition of the terrigenous end-member. A three-end-member mixing model is therefore required to more accurately evaluate the sources of OM deposited in the study area. The results of the mixing calculation indicate that terrigenous OM (soil-derived OM and vascular plant debris) accounts for similar to 79% of the OM deposited as inshore sediments and 66% of OM deposited as offshore sediments. Importantly, the abundance of terrigenous OM is 40% higher in inshore sediments and nearly 85% higher in offshore sediments than indicated by a two-end-member mixing model. Such a result highlights the need to reevaluate the inputs and cycling of soil-derived OM in the coastal ocean. Copyright (C) 2003 Elsevier Science Ltd.

Gordon, E. S. and M. A. Goni (2004). "Controls on the distribution and accumulation of terrigenous organic matter in sediments from the Mississippi and Atchafalaya river margin." *Marine Chemistry* **92**(1-4): 331-352.

Sediment samples from 14 box cores across the Mississippi and Atchafalaya River Margin were examined in order to quantify the magnitude and composition of the OM depositional flux in sediments from a river-dominated margin and identify the fate of terrigenous OM in the study area. Elemental, isotopic, mineral surface area, and terrigenous biomarker analyses suggest that physical sorting of particles across this river-dominated margin controls the chemical composition of sedimentary OM. Sediment accumulation rates in the area ranged from 0.012 to 0.68 cm/year and showed an inverse logarithmic relationship with water depth. Highest organic carbon (OC) content (1.3-1.5%) was observed on the inner shelf (<10 m water depth) and slope (>200 m water depth), with lower OC (0.8%) measured on the outer shelf (10-200 m water depth). Mineral surface area (SA) showed a similar spatial distribution as OC, with the highest values on the inner shelf (average 41 m²/g) and slope (average 54 m²/g), and low SA values (average 23 m²/g) on the outer shelf. Association of OM with minerals and its apparent differential transport across the study area results in the greatest proportion of OM accumulating on the inner shelf (37%), although the slope also plays a significant role in OM accumulation (33%) due to its greater areal extent. Stable organic carbon isotope ($\delta^{13}\text{C}(\text{OC})$) values ranged between -23 parts per thousand and -21 parts per thousand across the study area, with a slight seaward enrichment. The spatial trend in lignin yields mirrored that of $\delta^{13}\text{C}$, with a substantial decrease in lignin content from 1.8 mg/100 mg OC at inner shelf locations to 0.31 mg/100 mg OC at slope locations. The OC in all sediment samples exhibited more depleted radiocarbon compositions ($\Delta^{14}\text{C}(\text{OC})$) than modern values (>0 parts per thousand), ranging from ca. -200 parts per thousand on the inner shelf to ca. -400 parts per thousand on the slope. These isotopic and biomarker data indicate that terrigenous OM in the Gulf of Mexico is heterogeneous, composed of at least two sources: lignin-rich, isotopically depleted plant debris and lignin-poor, isotopically enriched soil-derived OM. The plant debris, which is deposited close to shore, composes a small portion of inner

shelf sediments. Soil-derived OM is deposited throughout the study area, although it appears to be preferentially transported to deeper regions. The fate of terrigenous OM in the northern Gulf of Mexico appears to be governed by the hydrodynamic sorting of riverine particles of different compositional character rather than by simple dilution with marine OM. (C) 2004 Elsevier B.V. All rights reserved.

Gordon, E. S., M. A. Goni, et al. (2001). "Organic matter distribution and accumulation on the inner Louisiana shelf west of the Atchafalaya River." Continental Shelf Research **21**(16-17): 1691-1721.

Surficial sediment samples from seven shallow cross-shelf transects west of the Atchafalaya River in the northern Gulf of Mexico were analyzed during three sampling periods to determine the distribution of organic matter along the shelf and to evaluate the temporal variability of its deposition. Downcore sediment profiles from four sites, which represent 50-200yr of deposition, were also examined to assess long-term changes in organic matter accumulation in this region. The Atchafalaya "mud stream," which transports fine sediment westward parallel to the coastline, appears to play an important role in the transport of river-derived organic matter. In general, sedimentary organic carbon (%OC) and total nitrogen (%TN) decrease seaward within each transect and westward along the shelf. Atomic organic carbon: nitrogen (C/N) ratios indicative of a terrestrial source (> 20) are observed near the mouth of the river during each sampling period, but values along the remainder of the shelf fall within a narrow range (9-11) with no apparent offshore trends. Depleted stable carbon isotope ($\delta C-13$) values typical of C3 plant debris (-27 parts per thousand) are found near the river mouth and become more enriched (-22 to -21 parts per thousand) offshore. Organic matter distribution throughout much of the study area is similar during each sampling period, with significant seasonal differences close to the river mouth. Sediment, particulate organic carbon (POC), and particulate organic nitrogen (PON) budgets constructed for the study area reveal that 31 % of the sediment exported by the Atchafalaya River is presently deposited within the study area annually, while the organic matter burial rates in the same region represent only 21% and 22% of the riverine POC and PON inputs, respectively. The POC and PON budgets also suggest that the organic matter remineralized in the water column is of algal origin (C/ N = 7.2), whereas riverine organic matter (C/N = 10) appears to be respired within the sediments. The 22.7 g POC $m^{-2} yr^{-1}$ and 2.7 g PON $m^{-2} yr^{-1}$ buried in the study area account for similar to 5 % of the combined riverine and autochthonous OC and ON inputs to this region of the Louisiana shelf. (C) 2001 Elsevier Science Ltd. All rights reserved.

Grabowski, K. S., D. L. Knies, et al. (2004). "Carbon pool analysis of methane hydrate regions in the seafloor by accelerator mass spectrometry." Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms **223-24**: 435-440.

Accelerator mass spectrometry for C-14 was applied to the study of carbon pools associated with methane hydrate formations found in the seafloor at two

continental margin sites. The Gulf of Mexico (GOM) site contains thermogenically produced methane that is ancient and thus free of C-14. The Cascadia Margin site contains biogenically produced methane, so may contain some C-14. This work reports on the C-14 content of organic matter in the sediment at the GOM site, and of the methane in hydrates from both sites. In the GOM, the surface sediments contained ancient organic matter that was from 20% to 60% of the total organic carbon content. At both sites, the collected hydrates contained essentially no C-14. (C) 2004 Elsevier B.V. All rights reserved.

Green, R. E., T. S. Bianchi, et al. (2006). "An organic carbon budget for the Mississippi River turbidity plume and plume contributions to air-sea CO₂ fluxes and bottom water hypoxia." Estuaries and Coasts **29**(4): 579-597.

We investigated seasonal variability in organic carbon (OC) budgets using a physical-biological model for the Mississippi River turbidity plume. Plume volume was calculated from mixed layer depth and area in each of four salinity subregions based on an extensive set of cruise data and satellite-derived suspended sediment distributions. These physical measurements were coupled with an existing food web model to determine seasonally dependent budgets for labile (reactive on time scales of days to weeks) OC in each salinity subregion. Autochthonous gross primary production (GPP) equaled 1.3×10^{12} g C yr⁻¹ and dominated labile OC inputs (88% of the budget) because riverine OC was assumed mostly refractory (nonreactive). For perspective, riverine OC inputs amounted to 3.9×10^{12} g C yr⁻¹, such that physical inputs were 3 times greater than biological inputs to the plume. Annually, microbial respiration (R) accounted for 65% of labile OC losses and net metabolism (GPP - R) for the entire plume was autotrophic, equaling 5.1×10^{11} g C yr⁻¹. Smaller losses of labile OC occurred via sedimentation (20%), advection (10%), and export to higher trophic levels (5%). In our present model, annual losses of labile OC are 10% higher than inputs, indicating future improvements are required. Application of our model to estimate air-sea carbon dioxide (CO₂) fluxes indicated the plume was a net sink of 2.0×10^8 mol CO₂ yr⁻¹, of which 90% of the total drawdown was from biotic factors. In all seasons, low salinity waters were a source of CO₂ (PCO₂ = 560-890 μatm), and intermediate to high salinity waters were a sink of CO₂ (PCO₂ = 200-370 μatm). Our model was also used to calculate O₂ demand for the development of regional hypoxia, and our spring and early summer budgets indicated that sedimentation of autochthonous OC from the immediate plume contributed 23% of the O₂ demand necessary for establishment of hypoxia in the region.

Gu, B., D. M. Schell, et al. (2001). "Stable carbon isotope evidence for reduced feeding of Gulf of Mexico sturgeon during their prolonged river residence period." Estuarine Coastal and Shelf Science **53**(3): 275-280.

Stable carbon isotope ratios were used to delineate food sources for Gulf of Mexico sturgeon (*Acipenser oxyrinchus desotoi*), an anadromous fish that migrates between Gulf of Mexico and the coastal rivers in south-east U.S.A. The large difference in isotope ratios (similar to 11 parts per thousand) between

freshwater food sources and fish muscle tissue suggests that the Gulf of Mexico sturgeon do not feed significantly in fresh waters. Isotope ratio data from this study and also from the literature indicate that the growth of Gulf of Mexico sturgeon is almost entirely supported by coastal marine food sources. It is likely that Gulf of Mexico sturgeon use the cool springs that seep into the river as a thermal refuge during their river residence in summer and that thermal barriers may prevent the fish from exploiting the rich food sources available in the warmer portions of the Suwannee River. (C) 2001 Academic Press.

Guo, L. D., C. H. Coleman, et al. (1994). "THE DISTRIBUTION OF COLLOIDAL AND DISSOLVED ORGANIC-CARBON IN THE GULF-OF-MEXICO." Marine Chemistry **45**(1-2): 105-119.

Cross-flow ultrafiltration techniques have been used to extract colloidal organic carbon (COC) from seawater and to investigate different molecular weight fractions of dissolved organic carbon (DOC). Using a high-temperature catalytic oxidation (HTCO) method, DOC and COC of seawater in the Gulf of Mexico were measured during a R/V Gyre cruise in June 1992. DOC concentrations in surface water varied from 131 μM at a near-shore station (water depth approximately 20 m) to 83 μM at an off-shore station (water depth approximately 1550 m). DOC concentrations show statistically significant correlations with apparent oxygen utilization (AOU), as well as with temperature. However, as an upper limit, only 20-30% of the oxygen consumption could be due to dissolved organic carbon oxidation. Furthermore, a good correlation between DOC and AOU existed only in the upper water column across the pycnocline, which we ascribed to lateral exchange processes. Water mixing can be quite important in controlling the distribution of DOC and the relationship between DOC and AOU in the water column. Concentrations of COC > 1000 Dalton ranged from 20 to 69 μM , while COC > 10,000 Dalton ranged from 4 to 16 μM in the study area. On average, COC (> 1000 Dalton) comprised about 45% of the initial DOC, and the mass concentration of colloids was > 1 mg l⁻¹. This was one order of magnitude higher than the concentration of suspended particulate matter, and indicates that COC may be an important component of the carbon cycle in the ocean. The relative abundance of COC (both > 1000 and > 10,000 Dalton) decreased from surface water to deep water, not only in terms of concentration but also relative to total DOC. The measurement of molecular weight distributions indicated that approximately 35% of the initial DOC was in the 1000-10,000 Dalton fraction, while only about 10% was in the > 10,000 Dalton fraction, leaving approximately 55% in the truly dissolved fraction (i.e. < 1000 Dalton).

Guo, L. D., C. C. Hung, et al. (2002). "Th-234 scavenging and its relationship to acid polysaccharide abundance in the Gulf of Mexico." Marine Chemistry **78**(2-3): 103-119.

Size-fractionated particulate Th-234 and acid polysaccharides (APS) were collected from stations along a transect in the Gulf of Mexico, in order to examine the role of APS content in controlling the extent and rates of Th-234 scavenging in the ocean and to explore, for the first time, the relationship between Th scavenging and biochemical composition of particulate matter.

Oceanographically consistent vertical profiles of dissolved and particulate Th-234 concentrations were observed, with a considerable Th-234 deficit relative to U-238 in the upper water column and in benthic nepheloid layers, but reaching secular equilibria between Th-234 and U-238 in intermediate waters. Within the total particulate Th-234 pool (>0.5 μm), the 10-53 μm fraction had the largest share of Th-234 (37-57%), followed by the >53 μm (13-36%), the 1 - 10 μm (10-21%), and the 0.5-1 μm (8-17%) fractions, resulting in a decrease of POC/(234) Th ratios with increasing particle size. Residence times of Th-234 in size-fractionated particles, calculated with a serial multi-box model, were, as expected, consistently shorter than those for total particulate Th-234, with the shortest residence times (< 0.5 day at coastal stations and < 1 - 5 days at deep stations) observed in the smaller particulate fractions (0.5- 10 μm), and the large particles >53 μm . These results suggest that submicron and micronsized particles are the most important intermediary in the Th scavenging and that Th-234 on smaller particles (< 10 μm) can coagulate into the 10-53 μm particles very rapidly, within a time scale of < 1 day. A positive correlation between Th-234/POC and OC-normalized total APS content was observed, suggesting that exopolymeric fibrillar APS, the surface active substances in seawater, are the most effective organic compounds for Th(IV) scavenging. Most importantly, residence times of particles in the size ranges of 1-10 and the >53 μm were also significantly and inversely correlated with uronic acid (URA, a fraction of total APS) concentrations, indicating that the APS content controls not only rates and amounts of Th-234 sorption, but also rates of coagulation of particles. Thus, the biochemical composition of marine particles needs to be considered in improved Th(IV) scavenging models. (C) 2002 Elsevier Science B.V All rights reserved.

Guo, L. D. and P. H. Santschi (1997). "Composition and cycling of colloids in marine environments." Reviews of Geophysics **35**(1): 17-40.

Colloidal (COM) or macromolecular organic matter makes up a significant portion of the bulk dissolved organic matter (DOM) pool in aquatic environments. Because of their high specific surface areas and complexation capacities, marine colloids are of great importance not only in the global carbon cycle but also in the biogeochemical cycling of many particle-reactive nuclides and trace elements in the ocean. However, the colloidal pool as a whole is still poorly understood and largely uncharacterized. Recently, cross-flow ultrafiltration and other separation techniques, which have been successfully used to isolate marine colloids, combined with a multitracer approach, have greatly advanced our understanding of the cycling of COM and its associated trace elements in marine environments. In this paper we focus on recent developments on isotopic and elemental composition of colloids which allow organic matter cycling in marine environments to be constrained. Major sections review sampling techniques for aquatic colloids, concentrations and distribution of COM, biochemical and elemental (organic and inorganic) characterization, and stable isotopic (C-13 and N-15) and radioisotopic (C-14 and Th-234) characterization of marine colloids. We discuss sources and turnover rates of organic matter in the ocean,

importance of benthic boundary layer processes in the cycling of DOM, changes in the paradigms of marine organic matter cycling, and research needs for a better understanding of the biogeochemistry of marine colloids.

Guo, L. D., P. H. Santschi, et al. (1997). "Interactions of thorium isotopes with colloidal organic matter in oceanic environments." Colloids and Surfaces a-Physicochemical and Engineering Aspects **120**(1-3): 255-271.

The phase speciation of thorium and consequences for the residence times of colloids have been examined in seawater of the Middle Atlantic Eight (MAB) and the Gulf of Mexico. Two fractions of colloidal organic matter (COM), $0.2 \mu\text{m} > \text{COM}(1) > 1 \text{ kD}$ and $0.2 \mu\text{m} > \text{COM}(10) > 10 \text{ kD}$, were sampled using cross-flow ultrafiltration techniques and measured for their Th-234 activity and organic carbon concentration. The ratios of mass concentrations of COM(1) to those of suspended particulate matter were as high as 10 in the MAB and 6-34 in the Gulf of Mexico. Higher concentrations of colloids may be of great importance in the biogeochemical cycling of many particle-reactive nuclides or trace elements owing to their high specific surface area and complexation capacity. A significant fraction of Th-234 in the traditionally defined "dissolved" pool was found to be associated with colloids. On average, about 10% of "dissolved" Th-234 was in the colloidal fraction of sizes between 10 kDa and $0.2 \mu\text{m}$, and similar to 50% was in the 1 kDa- $0.2 \mu\text{m}$ fraction. Values of the partition coefficients [K-c: $(0.5-4) \times 10(6) \text{ ml g}(-1)$ for K-c1 and $(0.5-7) \times 10(6) \text{ ml g}(-1)$ for K-c10] of Th-234 between truly dissolved ($<1 \text{ kDa}$) and colloidal fractions approximated those for Th-particle interactions [K-p: $(0.3-10) \times 10(6) \text{ ml g}(-1)$], indicating that colloid and suspended particle surface sites are similar. The distribution of Th-234 between dissolved, colloidal, and particulate phases was broadly similar to that of organic carbon in these oceanic environments. Thus, thorium isotopes might be used as tracers of marine organic carbon cycling. Residence times of colloids derived from Th-234:U-238 disequilibria were consistently short, ranging from 1 to 14 days for COM(10) and from 5 to 65 days for COM(1), suggesting that marine colloids are highly reactive in marine biogeochemical processes. The discrepancy between apparent turnover times of colloids ($>1 \text{ kDa}$) derived from Th scavenging and C-14 measurements suggest that Th-234 and C-14 may trace different geochemical pathways of colloids in the ocean.

Guo, L. D., P. H. Santschi, et al. (1996). "Cycling of high-molecular-weight dissolved organic matter in the middle Atlantic bight as revealed by carbon isotopic (C-13 and C-14) signatures." Limnology and Oceanography **41**(6): 1242-1252.

Carbon isotopes (C-13 and C-14) and elemental composition (C and N) in two fractions of colloidal organic matter (COM) were measured to study the origin and cycling of dissolved organic matter (DOM) in the Middle Atlantic Eight (MAE). COM(1) (1 kDa- $0.2 \mu\text{m}$) was 59% of the bulk DOM in surface Chesapeake Bay waters and decreased to 30-35% in waters of the MAB. COM(10) (10 kDa- $0.2 \mu\text{m}$), which was the high-molecular-weight (HMW) component of COM(1), comprised 3-12% of the bulk DOM, with highest concentrations in Chesapeake

Bay waters and the lowest in deep waters in the MAB. Delta(14)C values of COM(1) decreased from nearshore (-21 to +12 parts per thousand) to offshore and from surface (-166 to -85 parts per thousand) to bottom waters (-400 to -304 parts per thousand). Although Delta(14)C values of surface-water HMW COM(10) were generally high (-2 to -7 parts per thousand), values for bottom-water COM(10) were much lower (-129 to -709 parts per thousand). The high Delta(14)C values in the surface water suggest a particulate origin of pelagic COM, consistent with the contemporary Delta(14)C values of particulate organic matter (POM). The very low Delta(14)C values of bottom-water COM(10) imply that in addition to the pelagic origin, sedimentary organic C may serve as an important source for the benthic colloids in the bottom nepheloid layer. The general flow direction of organic carbon is from POM to HMW and to LMW DOM. Three colloidal end-members were identified in the MAB as well as in the Gulf of Mexico: estuarine colloids with high Delta(14)C values, high C:N ratios, and lower delta(13)C values; offshore surface water colloids with intermediate Delta(14)C values, lower C:N ratios, and higher delta(13)C values; and offshore deep-water colloids with low Delta(14)C values, intermediate C:N ratios, and variable delta(13)C values.

Guo, L. D., P. H. Santschi, et al. (1995). "Dynamics of dissolved organic carbon (DOC) in oceanic environments." Limnology and Oceanography **40**(8): 1392-1403.

Cross-flow ultrafiltration techniques and a high-temperature combustion (HTC) method were used to investigate the distributions and fluxes of dissolved (DOC) and colloidal organic carbon (COC) in the Gulf of Mexico and in the Middle Atlantic Bight. Concentrations of DOC in both regions decreased from less than or equal to 80 μM in surface waters to similar to 45 μM in deep waters and showed large vertical gradients in the subsurface layer. The vertical distributions of DOC were oceanographically consistent. A conservative mixing behavior of DOC was observed in slope waters, and water mixing processes were important factors in controlling the distribution of DOC in the ocean. Calculated downward fluxes of DOC are comparable to those measured for particulate organic C. Size fractionation results revealed that COC1 (1 kDa-0.2 μm) comprised similar to 40-50% of the total DOC in seawater off Cape Hatteras, while it comprised similar to 30-40% in the Gulf of Mexico. High-molecular-weight COC10 (10 kDa-0.2 μm) represented 4-10% of the total DOC in both study areas. Concentrations of COC1, COC3, and COC10 and their percentages in the total DOC decreased from nearshore to offshore and from surface to deep waters. The COC fractions seem to partition in a predictable way in seawater, with DOC concentration as a master variable. On average, 4-7% of the total DOC was in the COC10 fraction, 7-14% was in the 3-10-kDa fraction, and similar to 24% was in the 1-3-kDa Fraction, leaving 55-65% in the <1-kDa fraction.

Guo, L. D., N. Tanaka, et al. (2003). "Nitrogen and carbon isotopic composition of high-molecular-weight dissolved organic matter in marine environments." Marine Ecology-Progress Series **252**: 51-60.

High-molecular-weight (HMW) dissolved organic matter (DOM) was isolated

using cross-flow ultrafiltration from seawater across a salinity gradient in 2 estuarine/coastal marine environments-Chesapeake Bay/Middle Atlantic Bight (MAB) and Galveston Bay/Gulf of Mexico. Nitrogen and carbon isotope ratios ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}$) were measured on the isolated HMW DOM samples (defined here as the size fraction between 1 and 200 nm), which made up similar to 50 to 60 % of the total DOM in the estuarine regions and decreased to similar to 35 % of the DOM at the MAB and Gulf of Mexico stations. $\delta^{15}\text{N}$ values varied from 4.8 to 8.1 parts per thousand in the Chesapeake Bay/MAB area. In the Galveston Bay/Gulf of Mexico region, $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values varied from 3.2 to 9.5 parts per thousand and -26.1 to -20.9 parts per thousand, respectively. Similar distribution patterns of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ were observed in both study areas, with values of $\delta^{15}\text{N}$ showing a mid-salinity maximum of about 8 to 10 parts per thousand, whereas $\delta^{13}\text{C}$ continually increased with increasing salinity. The $\delta^{13}\text{C}$ values clearly demonstrated a shift of HMW organic carbon sources from largely terrestrial inputs in the upper-estuarine areas to marine-dominated organic carbon sources in lower-estuarine and coastal regions. The more complicated distribution patterns of $\delta^{15}\text{N}$, with $\delta^{15}\text{N}$ values first increasing with salinity in estuarine regions then decreasing towards the seawater endmember, suggest more dynamic N cycling. Thus, in addition to organic matter sources, biogeochemical and isotopic fractionation processes are important factors governing marine HMW DOM $\delta^{15}\text{N}$ values. Vertical profiles of HMW DOM $\delta^{13}\text{C}$ in open-ocean stations generally decrease from surface water to deep waters, whereas the opposite was found for $\delta^{15}\text{N}$. HMW DOM components with heavier $\delta^{13}\text{C}$ and lighter $\delta^{15}\text{N}$ values seem to be preferentially degraded during their transport from surface to deep waters. However, other processes could also have contributed to this distribution trend. While the carbon isotopic signature can be used as an indicator of DOM sources, nitrogen isotopic composition, on the other hand, appears to be related to both source functions and subsequent recycling in marine environments. Comparisons of $\delta^{15}\text{N}$ with previously published $\delta^{14}\text{C}$ values for the same samples support these conclusions about possible N-15 degradation pathways.

Hanson, P. J., C. C. Koenig, et al. (2004). "Elemental composition of otoliths used to trace estuarine habitats of juvenile gag *Mycteroperca microlepis* along the west coast of Florida." Marine Ecology-Progress Series **267**: 253-265.

The spatial relationships and relative contributions of known juvenile gag *Mycteroperca microlepis* habitats to specific fishery grounds and populations along the Florida west coast are virtually unknown. To determine if otolith composition is a valid tracer of specific nursery sites and can be used to classify adult fish to their nursery area, chemical concentrations in juvenile gag otoliths (Li, Na, K, Mg, Ca, Sr, Ba, Mn, Cu, Pb, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$,) were measured for 4 nursery areas along the Florida west coast in 1992, 1995 and 1996. Classification of fish to nursery area was by parametric discriminant function analysis and neural network simulation; both gave similar results in the spatial and temporal patterns of classification error and in identification of

important classification variables (Mn, Sr and $\delta^{13}\text{C}$). Classification success rates ranged from 66 to 100%. Interannual variability in otolith composition had a negative effect on classification success rate at the spatial scale of site separation (< 200 km). At regional spatial scales (> 300 km) the year effect was reduced and classification success remained high without consideration of year class. Analysis of classification errors supports the separation of sites into northern and southern groups. The observed negative trend in otolith Sr and positive trend in otolith Mn with increasing latitude are positively correlated with corresponding trends in groundwater Sr and sediment Mn, respectively, which are hypothesized to be the proximal causes for the otolith trends. Otolith composition is a valid technique for classifying juvenile gag to estuarine habitats along the west coast of Florida. Classification error rates of less than 10% are obtained when the year class of the fish is considered. Similar error rates were achieved across multi-year data at regional spatial scales.

Hernandez, M. E. and W. J. Mitsch (2007). "Denitrification in created riverine wetlands: Influence of hydrology and season." *Ecological Engineering* **30**(1): 78-88.

Created riverine wetlands play an important role in nitrate removal from non-point source pollution. In this study, we investigated the effect of flooding frequency on seasonal denitrification rates in two created riverine wetlands in the Midwest USA receiving controlled hydrologic pulses. Denitrification was measured using the in situ acetylene block technique; sampling plots were distributed in a longitudinal gradient, i.e., along the water flow and in a transverse gradient from the edge to the center of the wetlands. Flood frequency plots in the transverse gradient were influenced by hydrological pulses as follows: low marsh and open water zones were permanently flooded, high marsh zones had permanently saturated soils, but standing water during pulses, and edge zones were normally dry with standing water during flood pulses. Denitrification was significantly correlated with soil temperature in all plots and with growing season nitrate concentrations in the inflow surface water in permanently flooded plots. Late spring denitrification rates in the high marsh zone were significantly higher under flood pulsing ($778 \pm 92 \mu\text{gN m}^{-2} \text{h}^{-1}$) than under steady flow ($328 \pm 63 \mu\text{gN m}^{-2} \text{h}^{-1}$). In the low marsh and edge zones, flood pulses did not affect denitrification. $\text{N}_2\text{O}/\text{N}_2$ ratios were higher in intermittently flooded (high marsh and edge) zones than in permanently flooded (low marsh) zones and ratios increased in the cold seasons. Highest mean denitrification rates were observed in the low marsh zone ($800 \pm 102 \mu\text{gN m}^{-2} \text{h}^{-1}$) and they were significantly higher ($P < 0.05$) than in the high marsh ($458 \pm 87 \mu\text{gN m}^{-2} \text{h}^{-1}$) and edge ($315 \pm 40 \mu\text{gN m}^{-2} \text{h}^{-1}$) zones, but not significantly different from the open water zone ($584 \pm 101 \mu\text{gN m}^{-2} \text{h}^{-1}$). Denitrification in high marsh zones was not significantly different than in the open water and edge zones. In permanently flooded areas, denitrification rates were significantly higher near the wetland inflow than near the outflow, which was related to nitrate concentrations in the water column. Denitrification appeared to be nitrogen-limited in the low marsh, high marsh, and edge plots, but both carbon- and nitrogen-limited in open water. Flood frequency, nitrate availability,

and soil temperature were important factors controlling denitrification rates in these created wetlands. (c) 2007 Elsevier B.V. All rights reserved.

Hernandez-Ayon, J. M., A. Zirino, et al. (2007). "Estimating the contribution of organic bases from microalgae to the titration alkalinity in coastal seawaters." Limnology and Oceanography-Methods **5**: 225-232.

This study reports the potential contribution of organic bases to the alkalinity of seawater samples. The concentration of organic bases in these samples was inferred from the difference between the measured alkalinity and that calculated from a knowledge of pH and concentrations of the various inorganic acid- bases species such as total carbon, total boron, and so on. Significant concentrations of such organic bases were measured in cultures of the marine microalgae *Rhodomonas* sp. (800 $\mu\text{mol kg}^{-1}$) and *Isochrysis* aff. *Galbana* (400 $\mu\text{mol kg}^{-1}$), as well as in three marine environments (northern gulf of California, Mexico; San Quintin Bay, B. C., Mexico; and San Diego Bay). These three sites are characterized by significant biological activity and restricted mixing, and the organic bases were found at concentrations greater than 50 $\mu\text{mol kg}^{-1}$ in each of these three locations.

Hewson, I., J. A. Steele, et al. (2006). "Temporal and spatial scales of variation in bacterioplankton assemblages of oligotrophic surface waters." Marine Ecology-Progress Series **311**: 67-77.

Marine bacterioplankton dominate microbial carbon biomass in surface waters of the oligotrophic ocean, yet there have been few studies examining rates of change in bacterioplankton assemblage composition in situ over time and across water masses. Temporal changes in bacterioplankton assemblage composition were investigated during 7 drifter studies of 24 to 360 h duration in the oligotrophic Gulf of Mexico, the North Pacific and the West Tropical Atlantic in 2001 to 2003, using an assemblage fingerprinting technique, automated rRNA intergenic-spacer analysis (ARISA). The similarity indices between assemblages collected over time in the same drifter changed on average by a Sorensen index of 0.12 d^{-1} (comparing the presence/absence of operational taxonomic units, OTU) and a Whittaker index (comparing proportions in various OTU) of 0.17 d^{-1} per fingerprint, across all surface drifter studies. Fingerprints generated from 7 replicate bacterioplankton DNA samples collected at each of 2 stations were remarkably similar to each other, sharing a Whittaker index > 0.85 . Despite this consistency over small spatial scales (< 2 km), no clear relationship was observed between the separation distance of sampling locations and similarity between assemblage fingerprints in the North Pacific and Atlantic gyres over mesoscales (10 to 3000 km), oscillating around a mean of 0.38 to 0.47 for each gyre. Our results suggest that factors ultimately shaping assemblage composition are localized at spatial scales between a few kilometers and about 50 km, i.e. this is a typical horizontal 'patch size', within which communities are relatively homogenous, perhaps because physical mixing (e.g. by eddies) may dominate over biological interactions. Our results also suggest that, while similar environmental factors may cause bacterioplankton assemblages to share a small

portion of OTU between different sampling locations, biological factors selecting for particular bacterial types (e.g. viral lysis, grazing, antagonism, nutrition) may cause assemblage composition variability over short geographic distances.

Holmes, M. E., F. J. Sansone, et al. (2000). "Methane production, consumption, and air-sea exchange in the open ocean: An evaluation based on carbon isotopic ratios." Global Biogeochemical Cycles **14**(1): 1-10.

The concentration of methane and its isotopic composition did not appear to vary significantly in the subtropical North Pacific during 1996-1997. Methane enters the atmosphere via the upper mixed layer at a rate of $1.6 \mu\text{mol m}^{-2} \text{d}^{-1}$ (± 0.1) with a $\delta^{13}\text{C}$ value of approximately -42 parts per thousand (± 1.5), with no apparent seasonal variation. In comparison, the sea-air flux of methane in the Sargasso Sea was between 1.6 and $4.4 \mu\text{mol m}^{-2} \text{d}^{-1}$ with an isotopic composition between -43 and -45 parts per thousand. Excess methane in surface waters appears to be generated throughout the upper 300 m of the water column by bacterial methanogenesis. The methane concentration maxima occur at the pycnocline, suggesting that the maxima are supported by methanogenesis in suspended particles that accumulate at these depths. Particle incubation experiments show that methane production may occur in these microenvironments. The lack of a diurnal signal implies that methane production and consumption in the ocean is independent of day-night cycles such as photosynthesis, grazing and vertical migration of zooplankton. The flux to the atmosphere appears to be the main sink for methane in the upper ocean; microbial oxidation and downward eddy diffusion account for only 3 and 6%, respectively, of the total methane loss from the upper 300 m. Below that depth, concentrations decrease and isotopic ratios vary with depth due to bacterial oxidation and mixing of water masses of different ages and different histories of methane input.

Holtvoeth, J., T. Wagner, et al. (2003). "Organic matter in river-influenced continental margin sediments: The land-ocean and climate linkage at the Late Quaternary Congo fan (ODP Site 1075)." Geochemistry Geophysics Geosystems **4**.

Late Quaternary sections (1.2 Ma) of ODP-Site 1075 from the Congo deep-sea fan are investigated to reconstruct variations of terrigenous organic matter supply to the eastern equatorial Atlantic. To characterize the organic matter (OM) with regard to marine and terrigenous amounts we used elemental analysis (C, N, S), stable carbon isotopes (bulk $\delta^{13}\text{C}(\text{org})$), Rock-Eval pyrolysis, and terrigenous biomarkers (lignin phenols from CuO oxidation). The records of total organic carbon (TOC) contents, C-org/N-tot ratios, bulk OM degradation rates (C-org/C-org*), and the ratios of hydrocarbons (HC) from low-mature versus HC from high-mature OM (lm/hm) reveal pronounced cyclic changes in OM abundance, preservation, and reactivity that are closely related to the precessional controlled record of insolation, and thus, to variations in upwelling intensity and fluvial run-off. Primary productivity off the Congo is stimulated by both, enhanced nutrient supply in response to trade-induced upwelling during arid African climates (insolation minima) and fluvial nutrient delivery during humid

stages (following insolation maxima), especially due to the contribution of dissolved silica that is taken up preferably by diatoms. However, results stemming from a multiparameter approach reveal that the fluvial supply of degraded OM and black carbon (BC) associated with fine-grained sediments from soil erosion is a decisive factor for the preservation of marine OM and, in addition, significantly influences the geochemical signature of bulk and terrigenous OM. Riverine and eolian supply of C-4 plant matter, as well as enhanced concentrations of BC, during arid and arid-to-humid transitional climate stages, may lead to a severe underestimation of terrigenous organic carbon, if its amount is calculated from bulk isotopic ratios using binary end-member models. During the humid stages, it is the massive supply of C-13-enriched soil OM with low C-org/N-tot ratios that may suggest a mainly marine composition of bulk OM. In fact, terrigenous OM governs bulk OM geochemical signatures in the sediments of the Congo deep-sea fan, a result that is contradictory to earlier studies, especially to the conventional interpretation of the bulk $\delta(13)\text{C}(\text{org})$ signal.

Hopmans, E. C., J. W. H. Weijers, et al. (2004). "A novel proxy for terrestrial organic matter in sediments based on branched and isoprenoid tetraether lipids." Earth and Planetary Science Letters **224**(1-2): 107-116.

We propose a novel tracer for terrestrial organic carbon in sediments based on the analysis of tetraether lipids using high-performance liquid chromatography/mass spectrometry (HPLC/MS). Analysis of terrestrial soil and peats shows that branched tetraether lipids are predominant in terrestrial environments in contrast to crenarchaeol, the characteristic membrane lipid of non-thermophilic crenarchaeota, which is especially abundant in the marine and lacustrine environment. Based on these findings, an index was developed, the so-called Branched and Isoprenoid Tetraether (BIT) index, based on the relative abundance of terrestrially derived tetraether lipids versus crenarchaeol. This BIT index was applied to surface sediments from the Angola Basin, where it was shown to trace the outflow of the Congo River. Furthermore, analyses of particulate organic matter from the North Sea showed relatively higher BIT indices in water column particulate organic matter near large river inputs. A survey of globally distributed marine and lacustrine surface sediments shows that the BIT index in these environments correlates with the relative fluvial input of terrestrial organic material making this index generally applicable. The new proxy allows the rapid assessment of the fluvial input of terrestrial organic material in immature sediments up to 100 Ma old. (C) 2004 Elsevier B.V. All rights reserved.

Howarth, R. W. and R. Marino (2006). "Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: Evolving views over three decades." Limnology and Oceanography **51**(1): 364-376.

The first special volume of *Limnology and Oceanography*, published in 1972, focused on whether phosphorus (P) or carbon (C) is the major agent causing eutrophication in aquatic ecosystems. Only slight mention was made that estuaries may behave differently from lakes and that nitrogen (N) may cause

eutrophication in estuaries. In the following decade, an understanding of eutrophication in estuaries proceeded in relative isolation from the community of scientists studying lakes. National water quality policy in the United States was directed almost solely toward P control for both lakes and estuaries, and similarly, European nations tended to focus on P control in lakes. Although bioassay data indicated N control of eutrophication in estuaries as early as the 1970s, this body of knowledge was treated with skepticism by many freshwater scientists and water-quality managers, because bioassay data in lakes often did not properly indicate the importance of P relative to C in those ecosystems. Hence, the bioassay data in estuaries had little influence on water-quality management. Over the past two decades, a strong consensus has evolved among the scientific community that N is the primary cause of eutrophication in many coastal ecosystems. The development of this consensus was based in part on data from whole-ecosystem studies and on a growing body of evidence that presented convincing mechanistic reasons why the controls of eutrophication in lakes and coastal marine ecosystems may differ. Even though N is probably the major cause of eutrophication in most coastal systems in the temperate zone, optimal management of coastal eutrophication suggests controlling both N and P, in part because P can limit primary production in some systems. In addition, excess P in estuaries can interact with the availability of N and silica (Si) to adversely affect ecological structure. Reduction of P to upstream freshwater ecosystems can also benefit coastal marine ecosystems through mechanisms such as increased Si fluxes.

Hung, C. C., L. D. Guo, et al. (2004). "Upper ocean carbon flux determined by the Th-234 approach and sediment traps using size-fractionated POC and Th-234 data from the Gulf of Mexico." Geochemical Journal **38**(6): 601-611.

Size-fractionated particulate Th-234 and particulate organic carbon (POC) fluxes were measured in the Gulf of Mexico during 2000 and 2001 in order to obtain a better estimation of upper ocean organic carbon export out of the euphotic zone within cold core and warm core rings, and to assess the relative merit of sediment trap and POC/Th-234 methods. In 2000, the flux of POC measured by sediment traps at 120 m ranged from 60 to 148 mg C m⁻²d⁻¹, while Th-234-derived POC fluxes in large particles (>53 μm) varied from 18 to 61 mg C m⁻²d⁻¹ using the ratio of POC/Th-234 at 120 m, and from 51 to 163 mg C m⁻²d⁻¹ using an average ratio of POC/Th-234 for the upper 120 m water column. In 2001, the fluxes of POC measured by traps deployed at 120 m water depth ranged from 39 to 48 mg C m⁻²d⁻¹, while the Th-234-derived POC fluxes in large particles (>53 μm) varied from 7 to 37 mg C m⁻²d⁻¹ using a ratio of POC/Th-234 at 120 m, and from 37 to 45 mg C m⁻²d⁻¹ using an average ratio of POC/Th-234 within the 0-120 m interval. The results show that POC fluxes estimated by the ²³⁴Th method using the average ratio of POC/Th-234 within the euphotic zone are similar to those measured by sediment traps. Furthermore, the results demonstrate that the variability in POC export fluxes estimated by the Th-234/U-238 disequilibrium approach is strongly related to the ratio of POC/Th-234 that is taken, and for which we have independent evidence that it

may be controlled by the chemical composition of the suspended particles. The results also reveal that using POC/Th-234 ratios in small particles may result in an estimate of the POC export flux that is considerably higher than when using POC/ Th-234 ratios in large particles (>53 μm). The POC flux calculated from ratios in large particles is, however, more comparable to the POC flux determined directly by sediment traps, but both of these estimates are much lower than that determined by using the POC/Th-234 ratios in sinking particles. Therefore, without reliable flux values to compare with, Th-234-based and sediment trap approaches are complementary methods for estimating upper ocean POC export, with comparable uncertainties for both of these approaches.

Hung, C. C., L. D. Guo, et al. (2003). "Production and flux of carbohydrate species in the Gulf of Mexico." Global Biogeochemical Cycles **17**(2).

[1] Carbohydrates are an important organic compound class in seawater and play an active role in the biogeochemical cycling of organic carbon and trace elements in the ocean, but are poorly characterized. To better understand the sources and role of carbohydrate species in marine environments, the concentrations and fluxes of particulate carbohydrates (CHO), total acid polysaccharides (APS), uronic acids (URA), phytoplankton composition and bacterial production were measured in the Gulf of Mexico in 2000 and 2001. A strong positive correlation between APS concentration and cyanobacteria abundance was found in 2000. In 2001, prymnesiophyte abundance correlated well with both concentrations of APS and URA. Bacterial production data, measured simultaneously in 2001, showed significant positive relationships with particulate organic carbon (POC), CHO, APS and URA concentrations, respectively. The average fluxes out of the euphotic zone of CHO, APS and URA in 2000 were 8.1, 1.3, and 0.7 mg C m⁻² d⁻¹, respectively. In 2001, the average fluxes of CHO, APS and URA were about 3 times higher than those in 2000, which was a time of lower nutrient concentrations, indicating that the fluxes of carbohydrate species are related to the nutrient status and phytoplankton composition. The results suggest that APS in the upper water column can be produced by cyanobacteria, prymnesiophytes, and heterotrophic bacteria. Most importantly, our data indicate that APS and CHO compounds are more resistant to biological degradation than other organic compounds, suggesting that the role of CHO compounds in carbon cycling in the ocean is more complex than previously thought.

Inwood, S. E., J. L. Tank, et al. (2007). "Factors controlling sediment denitrification in midwestern streams of varying land use." Microbial Ecology **53**(2): 247-258.

We investigated controls on stream sediment denitrification in nine headwater streams in the Kalamazoo River Watershed, Michigan, USA. Factors influencing denitrification were determined by using experimental assays based on the chloramphenicol-amended acetylene inhibition technique. Using a coring technique, we found that sediment denitrification was highest in the top 5 cm of the benthos and was positively related to sediment organic content. To determine the effect of overlying water quality on sediment denitrification, first-order stream

sediments were assayed with water from second- and third-order downstream reaches, and often showed higher denitrification rates relative to assays using site-specific water from the first-order stream reach. Denitrification was positively related to nitrate (NO₃) concentration, suggesting that sediments may have been nutrient-limited. Using stream -incubated inorganic substrata of varying size classes, we found that finer-grained sand showed higher rates of denitrification compared to large pebbles, likely due to increased surface area per volume of substratum. Denitrification was measurable on both inorganic substrata and fine particulate organic matter loosely associated with inorganic particles, and denitrification rates were related to organic content. Using nutrient-amended denitrification assays, we found that sediment denitrification was limited by NO₃ or dissolved organic carbon (DOC, as dextrose) variably throughout the year. The frequency and type of limitation differed with land use in the watershed: forested streams were NO₃-limited or colimited by both NO₃ and DOC 92% of the time, urban streams were more often NO₃-limited than DOC-limited, whereas agricultural stream sediments were DOC-limited or co-limited but not frequently limited by NO₃ alone.

Jahnke, L. L., R. E. Summons, et al. (1995). "IDENTIFICATION OF METHANOTROPHIC LIPID BIOMARKERS IN COLD-SEEP MUSSEL GILLS - CHEMICAL AND ISOTOPIC ANALYSIS." Applied and Environmental Microbiology **61**(2): 576-582.

A lipid analysis of the tissues of a cold-seep mytilid mussel collected from the Louisiana slope of the Gulf of Mexico was used in conjunction with a compound-specific isotope analysis to demonstrate the presence of methanotrophic symbionts in the mussel gill tissue and to demonstrate the host's dependence on bacterially synthesized metabolic intermediates. The gill tissue contained large amounts of group-specific methanotrophic biomarkers, bacteriohopanoids, 4-methylsterols, lipopolysaccharide-associated hydroxy fatty acids, and type I-specific 16:1 fatty acid isomers with bond positions at Delta 8, Delta 10, and Delta 11. Only small amounts of these compounds were detected in the mantle or other tissues of the host animal. A variety of cholesterol and 4-methylsterol isomers were identified as both free and sterol esters, and the sterol double bond positions suggested that the major bacterially derived gill sterol [11.0% 4 alpha-methyl-cholesta-8(14),24-dien-3 beta-ol] was converted to host cholesterol (64.2% of the gill sterol was cholest-5-en-3 beta-ol). The stable carbon isotope values for gill and mantle preparations were, respectively, -59.0 and -60.4 parts per thousand for total tissue, -60.6 and -62.4 parts per thousand for total lipids, -60.2 and -63.9 parts per thousand for phospholipid fatty acids, and -71.8 and -73.8 parts per thousand for sterols. These stable carbon isotope values revealed that the relative fractionation pattern was similar to the patterns obtained in pure culture experiments with methanotrophic bacteria (R. E. Summons, L. L. Jahnke, and Z. Roksandic, *Geochim. Cosmochim. Acta* 58:2853-2863, 1994) further supporting the conversion of the bacterial methylsterol pool.

Jasper, J. P. and R. B. Gagosian (1993). "THE RELATIONSHIP BETWEEN SEDIMENTARY ORGANIC-CARBON ISOTOPIC COMPOSITION AND ORGANIC BIOMARKER COMPOUND CONCENTRATION." Geochimica Et Cosmochimica Acta **57**(1): 167-186.

A study of organic biomarker compounds which could serve as tracers of terrigenous and marine sedimentary organic matter sources was performed on samples from a 208.7 m hydraulic piston core hole (DSDP Hole 619) from the hemipelagic Pigmy Basin in the northern Gulf of Mexico. Organic carbon-normalized concentrations of total long chain (C37-C39) alkenones and some individual C27-C29 desmethyl sterols were determined to be useful proportional indicators (tracers) of preserved marine and terrigenous organic carbon, respectively. The alkenones, whose only known source is marine phytoplankton of the class Prymnesiophyceae, generally occurred in higher concentrations in interglacial isotope stages 1 and 5a-b than in the intervening glacial stages. Sterols (C27-C29), apparently of a dominantly terrigenous origin, occurred in lower concentrations during interglacial stages than in glacial stages. Tracers of both terrigenous and marine organic matter appear to be affected by the differential diagenetic alteration of the biomarker/C(org) ratios, as indicated by a simple, first-order kinetic model. The lack of any desmethyl- or 4 α -methylsterol which is linearly related to the proportion of marine sedimentary organic matter (as scaled by $\delta^{13}\text{C}(\text{org})$) indicates that either (1) sedimentary diagenesis has obscured the biomarker/C(org) vs. $\delta^{13}\text{C}(\text{org})$ record, or (2) phytoplanktonic assemblage changes caused variations in the biomarker/C(org) ratio of the primary input. Preferential preservation of terrigenous sterols may result in a biased sedimentary record of sterol input which could be misinterpreted as indicating solely terrigenous sterol sources. A simple model which characterizes the effects of sedimentary diagenesis on the relationship between C(org)-normalized biomarker ratios and $\delta^{13}\text{C}(\text{org})$ demonstrates the potential problems of long-term, differential-diagenetic skewing on those tracer records.

Jasper, J. P. and J. M. Hayes (1993). "REFINED ESTIMATION OF MARINE AND TERRIGENOUS CONTRIBUTIONS TO SEDIMENTARY ORGANIC-CARBON." Global Biogeochemical Cycles **7**(2): 451-461.

Molecular carbon isotopic (C-13/C-12) ratios of a selected marine organic biomarker compound (a C37 alkadienone) from the Pigmy Basin (Deep Sea Drilling Program Hole 619) in the northern Gulf of Mexico varied by 5.3 parts per thousand in synchrony with the last approximately 100 ka glacial-interglacial cycle. This Carbon isotopic ($\delta^{13}\text{C}$) Variation is likely due to the effect of climatically linked variations in concentrations of $\text{CO}_2(\text{aq})$ on photosynthetic fractionation of carbon isotopes by phytoplankton. Measurement of the $\delta^{13}\text{C}$ of the alkadienone ($\delta^{37:2}$) to reconstruct the carbon isotopic composition of total marine organic carbon permits improved estimates of the time-varying $\delta^{13}\text{C}$ of preserved marine organic carbon end members. With the time series record of marine end members, the concentrations and net accumulation rates of terrigenous C(org) and marine C(org) are calculated and their paleoceanographic

significance is considered. Although this method may be improved by consideration of additional biomarkers representative of diverse marine and terrigenous inputs, it is the first application of molecular isotopic analysis to quantifying marine and terrigenous C(org) concentrations. Further application of such techniques will become valuable in reconstructing regional and global budgets of marine and terrigenous C(org) accumulation.

Jha, M., J. G. Arnold, et al. (2006). "Climate change sensitivity assessment on Upper Mississippi River Basin streamflows using SWAT." Journal of the American Water Resources Association **42**(4): 997-1015.

The Soil and Water Assessment Tool (SWAT) model was used to assess the effects of potential future climate change on the hydrology of the Upper Mississippi River Basin (UMRB). Calibration and validation of SWAT were performed using monthly stream flows for 1968-1987 and 1988-1997, respectively. The R-2 and Nash-Sutcliffe simulation efficiency values computed for the monthly comparisons were 0.74 and 0.69 for the calibration period and 0.82 and 0.81 for the validation period. The effects of nine 30-year (1968 to 1997) sensitivity runs and six climate change scenarios were then analyzed, relative to a scenario baseline. A doubling of atmospheric CO₂ to 660 ppmv (while holding other climate variables constant) resulted in a 36 percent increase in average annual streamflow while average annual flow changes of -49, -26, 28, and 58 percent were predicted for precipitation change scenarios of -20, -10, 10, and 20 percent, respectively. Mean annual streamflow changes of 51, 10, 2, -6, 38, and 27 percent were predicted by SWAT in response to climate change projections generated from the CISRO-RegCM2, CCC, CCSR, CISRO-Mk2, GFDL, and HadCM3 general circulation model scenarios. High seasonal variability was also predicted within individual climate change scenarios and large variability was indicated between scenarios within specific months. Overall, the climate change scenarios reveal a large degree of uncertainty in current climate change forecasts for the region. The results also indicate that the simulated UMRB hydrology is very sensitive to current forecasted future climate changes.

Jochem, F. J. (2003). "Photo- and heterotrophic pico- and nanoplankton in the Mississippi River plume: distribution and grazing activity." Journal of Plankton Research **25**(10): 1201-1214.

The abundance of pico- and nanophytoplankton, bacteria and heterotrophic nanoflagellates, and grazing rates on phototrophic pico- and nanoplankton and bacterioplankton were assessed along a salinity gradient (0.2-34.4) in the Mississippi River plume in May 2000. Grazing rates were established by serial dilution experiments, and analysis by flow cytometry allowed differentiation of grazing rates for different phytoplankton subpopulations (eukaryotes, *Synechococcus* spp., *Prochlorococcus* spp.). Grazing rates on phytoplankton tended to increase along the salinity gradient and often approached or exceeded 1 day⁻¹. Phytoplankton net growth rates (growth-grazing) were mostly negative, except for positive values for eukaryotic nanoplankton in the low-salinity,

high-chlorophyll region. Grazing pressure on bacteria was moderate (similar to 0.5 day^{-1}) and bacteria gained positive net growth rates of similar to 0.3 day^{-1} . Eukaryotic nanophytoplankton were the major phototrophic biomass and protozoan food source, contributing 30-80% of the total consumed carbon. Bacteria were the second most important food source at 9-48% of the total consumed carbon. *Synechococcus* spp. and *Prochlorococcus* spp. remained an insignificant portion of protozoan carbon consumption, probably due to their low contribution to the total pico- and nanoplankton biomass. Group-specific grazing losses relative to standing stocks suggest protozoan prey preference for eukaryotes over bacteria. Protozoan grazers exerted a major grazing pressure on pico- and nanophytoplankton, but less so on bacteria.

John, D. E., Z. H. A. Wang, et al. (2007). "Phytoplankton carbon fixation gene (RuBisCO) transcripts and air-sea CO₂ flux in the Mississippi River plume." Isme Journal **1**(6): 517-531.

River plumes deliver large quantities of nutrients to oligotrophic oceans, often resulting in significant CO₂ drawdown. To determine the relationship between expression of the major gene in carbon fixation (large subunit of ribulose-1,5-bisphosphate carboxylase/oxygenase, RuBisCO) and CO₂ dynamics, we evaluated *rbcL* mRNA abundance using novel quantitative PCR assays, phytoplankton cell analyses, photophysiological parameters, and pCO₂ in and around the Mississippi River plume (MRP) in the Gulf of Mexico. Lower salinity (30-32) stations were dominated by *rbcL* mRNA concentrations from heterokonts, such as diatoms and pelagophytes, which were at least an order of magnitude greater than haptophytes, α -*Synechococcus* or high-light *Prochlorococcus*. However, *rbcL* transcript abundances were similar among these groups at oligotrophic stations (salinity 34-36). Diatom cell counts and heterokont *rbcL* RNA showed a strong negative correlation to seawater pCO₂. While *Prochlorococcus* cells did not exhibit a large difference between low and high pCO₂ water, *Prochlorococcus* *rbcL* RNA concentrations had a strong positive correlation to pCO₂, suggesting a very low level of RuBisCO RNA transcription among *Prochlorococcus* in the plume waters, possibly due to their relatively poor carbon concentrating mechanisms (CCMs). These results provide molecular evidence that diatom/pelagophyte productivity is largely responsible for the large CO₂ drawdown occurring in the MRP, based on the cooccurrence of elevated RuBisCO gene transcript concentrations from this group and reduced seawater pCO₂ levels. This may partly be due to efficient CCMs that enable heterokont eukaryotes such as diatoms to continue fixing CO₂ in the face of strong CO₂ drawdown. Our work represents the first attempt to relate in situ microbial gene expression to contemporaneous CO₂ flux measurements in the ocean.

Jorgensen, N. O. G., N. Kroer, et al. (1999). "Relations between bacterial nitrogen metabolism and growth efficiency in an estuarine and an open-water ecosystem." Aquatic Microbial Ecology **18**(3): 247-261.

Bacterial uptake or release of dissolved nitrogen compounds (amino nitrogen,

urea, ammonium and nitrate) were examined in 0.8 µm filtered water from an estuary (Santa Rosa Sound [SRS], northwestern Florida) and an open-water location in the Gulf of Mexico (GM). The bacterial nutrient dynamics were related to oxygen consumption and activity of enzymes involved in nitrogen assimilation (glutamate dehydrogenase [GDH], glutamine synthetase [GS] and aminopeptidase activity [leu-MCA]). Dissolved free amino acids (DFAA) were the dominant N source to the bacteria, followed by dissolved combined amino acids (DCAA), ammonium and nitrate. Nitrogen budgets of the bacteria (assimilation of N compounds relative to accumulated N biomass) demonstrated that, except for the initial 24 h period in the GM cultures, the assimilated N compounds sustained all of the bacterial N demand. Urea was released in both sets of cultures, but in the SRS cultures the produced urea was reassimilated. Major differences in the bacterial N metabolism between the open-water GM and the estuarine SRS stations were observed. Relative to the GM station, bacteria in the SRS cultures had (1) a 2.4 to 18x higher cell-specific DFAA assimilation, (2) a 2.5x higher cell-specific leu-MCA activity, (3) a 3 to 10x higher GDH:GS activity ratio and (4) a 1.9 to 4.1x lower cell-specific respiration. The larger nutrient availability at the estuarine station probably caused these differences in uptake and metabolism of nitrogen as well as the lower respiratory rate, relative to the open-water station. Therefore, we hypothesize that availability of nitrogen, rather than carbon, controlled the bacterial activity in the cultures. Our results suggest that bacteria in eutrophic conditions can be more important mediators of nitrogen than those in oligotrophic conditions, in which bacteria temporarily may immobilize labile nitrogen.

Joye, S. B., A. Boetius, et al. (2004). "The anaerobic oxidation of methane and sulfate reduction in sediments from Gulf of Mexico cold seeps." Chemical Geology **205**(3-4): 219-238.

We determined the geochemical characteristics of sediments and measured rates of the anaerobic oxidation of methane (AOM) and sulfate reduction (SR) in samples collected near thermogenic (structure II) gas hydrate mounds and in areas lacking hydrates along the continental slope in the Gulf of Mexico. We used radiotracer (C-14 and S-35) techniques to determine rates of AOM and SR over depth in sediment cores. Abundant mats of white and orange *Beggiatoa* spp. were common in areas of active seepage and these sediments were enriched in hydrogen sulfide and methane. In cores collected from areas without *Beggiatoa* or hydrate, concentrations of redox metabolites showed little variation over depth and these sites were inferred to be areas of low seepage. Integrated AOM rates were low in *Beggiatoa*-free cores (<0.05 mmol m⁻² day⁻¹) and averaged 2.8 ± 4.6 mmol m⁻² day⁻¹ in seep cores that contained *Beggiatoa* or gas hydrate. Integrated SR rates were also low in *Beggiatoa*-free cores (<1 mmol m⁻² day⁻¹) and averaged 54 ± 94 mmol m⁻² day⁻¹ in cores with *Beggiatoa* or hydrate. Rates of SR generally exceeded rates of AOM and the two processes were loosely coupled, suggesting that the majority of SR at Gulf of Mexico hydrocarbon seep sites is likely fueled by the oxidation of other organic matter, possibly other hydrocarbons and oil, rather than by AOM. (C) 2004

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Justic, D., N. N. Rabalais, et al. (1997). "Impacts of climate change on net productivity of coastal waters: implications for carbon budgets and hypoxia." Climate Research **8**(3): 225-237.

General circulation models predict that freshwater discharge from the Mississippi River (USA) to the coastal ocean would increase 20 % if atmospheric CO₂ concentration doubles. Here we use a coupled physical-biological 2-box model to investigate the potential impacts of increased freshwater and nutrient inputs on the production and decay of organic matter in the coastal waters of the northern Gulf of Mexico. Model results for a doubled CO₂ climate indicate that the annual net productivity of the upper water column (NP, 0 to 10 m) is likely to increase by 65 g C m⁻² yr⁻¹, relative to a 1985-1992 average (122 g C m⁻² yr⁻¹). Interestingly, this projected increase is of the same magnitude as the one that has occurred since the 1940s due to the introduction of anthropogenic nutrients. An increase in annual NP of 32 g C m⁻² yr⁻¹ was observed during the Great Mississippi River Flood of 1993, thus indicating the general validity of a doubled CO₂ scenario. The total oxygen uptake in the lower water column (10 to 20 m), in contrast, is likely to remain at its present value of about 200 g O₂ m⁻² yr⁻¹. Thus, carbon export and burial, rather than in situ respiration, are likely to be the dominant processes balancing coastal carbon budgets, leading perhaps to an expanded extent of the hypoxic zone.

Justic, D., N. N. Rabalais, et al. (2002). "Modeling the impacts of decadal changes in riverine nutrient fluxes on coastal eutrophication near the Mississippi River Delta." Ecological Modelling **152**(1): 33-46.

A mathematical model was used to link decadal changes in the Mississippi River nutrient flux to coastal eutrophication near the Mississippi River Delta. Model simulations suggest that bottom water hypoxia intensified about 30 years ago, as a probable consequence of increased net productivity and increased sedimentation of the organic material produced in situ in the upper water column. Model simulations also suggest that long-term increase in riverine nutrient fluxes has been responsible for this historical decrease in bottom layer oxygen concentrations. Importantly, model simulations are in good agreement with the available historical data from the northern Gulf of Mexico, and are additionally supported by the retrospective analyses of sedimentary records. Conclusively, this modeling study supports the hypothesis that riverine nutrient fluxes, via their influence on net productivity of the upper water column, play a major role in controlling the development of bottom water hypoxia and accumulation of organic carbon in coastal sediments. (C) 2002 Elsevier Science B.V. All rights reserved.

Kaldy, J. E., L. A. Cifuentes, et al. (2005). "Using stable isotope analyses to assess carbon dynamics in a shallow subtropical estuary." Estuaries **28**(1): 86-95.

The sources of carbon, which fuel water column respiration, remain unresolved for most estuaries; our objective was to examine carbon dynamics in a shallow subtropical estuary. We sampled the Sabine-Neches estuary, Texas, during low

(November 1999) and high (May 2000) freshwater inflow and measured stable carbon isotope ratios of the dissolved inorganic and organic carbon ($\delta^{13}\text{C-DIC}$, $\delta^{13}\text{C-DOC}$), as well as quantifying accessory parameters (salinity, nutrients, total suspended solids, and photosynthetic pigments). Pigment analysis indicated that diatoms were the predominant phytoplankton. Data from the May 2000 sampling event exhibited conservative mixing, indicating that the system was acting as a conduit between the watershed and the Gulf of Mexico. During November, mixing was generally nonconservative indicating extensive recycling of allochthonous and autochthonous carbon sources. Our data imply that both carbon sources had similar isotope ratios that made it impossible to unambiguously determine the dominant source supporting respiration. The nonconservative DIC concentration data indicating an autotrophic sink as well as the strong relationship between $\delta^{13}\text{C-DOC}$ and chlorophyll a, suggest that in situ production was an important component of the DOC pool. We hypothesize that uncharacteristically calm wind conditions during sampling may have promoted phytoplankton settling, removing autotrophs from the water column, but leaving behind a dissolved biogeochemical signature. Interpretation of carbon dynamics may be confounded by spatial and temporal decoupling of producers and consumers from biogeochemical indicators.

Kalish, J. E., C. P. Onuf, et al. (2002). "Carbon budget for a subtropical seagrass dominated coastal lagoon: How important are seagrasses to total ecosystem net primary production?" *Estuaries* **25**(4A): 528-539.

It has been assumed that because seagrasses dominate macrophyte biomass in many estuaries they also dominate primary production. We tested this assumption by developing three carbon budgets to examine the contribution of autotrophic components to the total ecosystem net primary production (TENPP) of Lower Laguna Madre, Texas. The first budget coupled average photosynthetic parameters with average daily irradiance to calculate daily production. The second budget used average photosynthetic parameters and hourly in situ irradiance to estimate productivity. The third budget integrated temperature-adjusted photosynthetic parameters (using $Q(10) = 2$) and hourly in situ irradiance to estimate productivity. For each budget TENPP was calculated by integrating production from each autotroph based on the producers' areal distribution within the entire Lower Laguna Madre. All budgets indicated that macroalgae account for 33-42% of TENPP and seagrasses consistently accounted for about 33-38%. The contribution by phytoplankton was consistently about 15-20%, and the contribution from the benthic microalgae varied between 8% and 36% of TENPP, although this may have been underestimated due to our exclusion of the within bed microphytobenthos component. The water column over the seagrass beds was net heterotrophic and consequently was a carbon sink consuming between 5% and 22% of TENPP. TENPP ranged between 5.41×10^{10} and 2.53×10^{11} g C yr⁻¹, depending on which budget was used. The simplest, most idealized budget predicted the highest TENPP, while the more realistic budgets predicted lower values. Annual production rates estimated using the third budget for *Halodule wrightii* and *Thalassia testudinum* compare

well with field data. Macroalgae and microalgae contribute 50-60% of TENPP, and seagrass may be more important as three-dimensional habitat (i.e., structure) than as a source of organic carbon to the water column in Lower Laguna Madre.

Kelley, C. (2003). "Methane oxidation potential in the water column of two diverse coastal marine sites." Biogeochemistry **65**(1): 105-120.

Methane oxidation in the water column was investigated at two nearshore marine environments with relatively high concentrations of dissolved methane. In the northern Gulf of Mexico, high methane oxidation rates were observed at the pycnocline, with the highest oxidation rate corresponding to the most negative bacterial $\delta(13)\text{C}$ values. These low isotopic values occurred during the winter when overall bacterial productivity was low, suggesting that at this time of the year, methanotrophs in the Gulf could make up a significant portion of the overall bacterial assemblage. Although methane oxidation also occurred during more productive times (i.e., summer), the isotopic signal of methane oxidation was not observed in the bacterial biomass because of the higher overall bacterial productivity. The other site, Cape Lookout Bight, NC, is a small marine embayment where methane is produced in the organic-rich sediments. No measurable rates of methane oxidation in the water column occurred, and no anomalously low $\delta(13)\text{C}$ values of the bacterioplankton were measured. In both environments, methane production and oxidation appear to be spatially coupled, occurring at/near the pycnocline in the northern Gulf of Mexico and at the sediment-water interface at Cape Lookout Bight, NC.

Kelley, C. A., R. B. Coffin, et al. (1998). "Stable isotope evidence for alternative bacterial carbon sources in the Gulf of Mexico." Limnology and Oceanography **43**(8): 1962-1969.

Kelley, C. A. and W. H. Jeffrey (2002). "Dissolved methane concentration profiles and air-sea fluxes from 41 degrees S to 27 degrees N." Global Biogeochemical Cycles **16**(3).

[1] Water column samples from a transect cruise from southern Chile through the Panama Canal to the Gulf of Mexico were used to determine dissolved methane depth profiles and air-sea methane fluxes. In the Gulf of Mexico, surface concentrations were approximately 40% supersaturated with respect to the atmosphere, whereas near the equator and in the Peru upwelling region, 10-20% supersaturation generally occurred. These saturation ratios translate into an average flux of methane from the sea surface to the atmosphere of $0.38 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$. In addition, water column profiles of dissolved methane indicate that subsurface maxima in dissolved methane concentrations are a consistent feature of the open ocean, except near the equator. At the equator, the subsurface peak at the base of the mixed layer may be bowed down by the Equatorial Undercurrent. The highest methane concentration (12 nM) was observed in the Peru upwelling region.

Kellogg, D. Q., A. J. Gold, et al. (2005). "In situ ground water denitrification in stratified,

permeable soils underlying riparian wetlands." Journal of Environmental Quality **34**(2): 524-533.

The ground water denitrification capacity of riparian zones in deep soils, where substantial ground water can flow through low-gradient stratified sediments, may affect watershed nitrogen export. We hypothesized that the vertical pattern of ground water denitrification in riparian hydric soils varies with geomorphic setting and follows expected subsurface carbon distribution (i.e., abrupt decline with depth in glacial outwash vs. negligible decline with depth in alluvium). We measured in situ ground water denitrification rates at three depths (65, 150, and 300 cm) within hydric soils at four riparian sites (two per setting) using a N-15-enriched nitrate "push-pull" method. No significant difference was found in the pattern and magnitude of denitrification when grouping sites by setting. At three sites there was no significant difference in denitrification among depths. Correlations of site characteristics with denitrification varied with depth. At 65 cm, ground water denitrification correlated with variables associated with the surface ecosystem (temperature, dissolved organic carbon). At deeper depths, rates were significantly higher closer to the stream where the subsoil often contains organically enriched deposits that indicate fluvial geomorphic processes. Mean rates ranged from 30 to 120 $\mu\text{g N kg}^{-1} \text{d}^{-1}$ within 10 m versus < 1 to 40 $\mu\text{g N kg}^{-1} \text{d}^{-1}$ at > 30 m from the stream. High denitrification rates observed in hydric soils, down to 3 m within 10 m of the stream in both alluvial and glacial outwash settings, argue for the importance of both settings in evaluating the significance of riparian wetlands in catchment-scale N dynamics.

Kennicutt, M. C. and J. M. Brooks (1990). "RECOGNITION OF AREAS EFFECTED BY PETROLEUM SEEPAGE - NORTHERN GULF-OF-MEXICO CONTINENTAL-SLOPE." Geo-Marine Letters **10**(4): 221-224.

The presence of large amounts of gas and/or liquid hydrocarbon seepage in near surface sediments can produce distinct features including an irregular topography (on several scales, ranging from meters to kilometers); seismically transparent/chaotic sediments; oil staining; gas plumes; sediments containing elevated concentrations of extractable organic matter, organic carbon, and calcium carbonate; associated brine seepage and anoxic conditions; extensive bacterial mats; hydrate formation and decomposition; and dense chemoautotrophic communities. Although no single characteristic is always uniquely associated with seepage, the co-occurrence of several of these features is strongly suggestive of an area being exposed to non-indigenous upward migrating hydrocarbons.

Kiene, R. P. and L. J. Linn (2000). "Distribution and turnover of dissolved DMSP and its relationship with bacterial production and dimethylsulfide in the Gulf of Mexico." Limnology and Oceanography **45**(4): 849-861.

We measured the distribution of particulate and dissolved pools of the phytoplankton osmolyte dimethylsulfoniopropionate (DMSP) in the euphotic zone at a series of shelf (<40 m total water depth) and oceanic (>500 m depth) stations in the northern Gulf of Mexico. We also measured turnover rates of the

dissolved DMSP pools (DMSPd) with tracer additions of S-35-DMSPd and short-term (<1 h) incubations, with the aim of examining the relationship between DMSPd turnover and bacterial production. Particulate DMSP concentrations were relatively low (<25 nM) throughout the study area with about twofold higher mean concentration at the shelf sites (15 nM) compared with the oligotrophic oceanic sites (7 nM). DMSPd concentrations averaged 3.0 nM in shelf waters and 1.3 nM in oceanic waters. Concentrations of dimethylsulfide (DMS), a degradation product of DMSP, also were low throughout the Gulf, averaging 2.0 nM for all depths sampled and 2.5 nM in surface waters. Microbial assemblages metabolized S-35-DMSPd with the sulfur being incorporated into biomass, volatile compounds (DMS and methanethiol), and other dissolved products. DMSPd turnover was relatively slow (mean of 3.8 nM d⁻¹) in oligotrophic oceanic waters and averaged 10-fold higher (39 nM d⁻¹) in mesotrophic shelf waters. DMS concentrations ranged from 0.2 to 5.1 nM in oceanic waters and appeared to be weakly related to DMSP turnover. In contrast, DMS concentrations in shelf waters fell within a narrow range (0.8-2.8 nM) and showed no relationship at all with DMSPd turnover. DMSPd turnover rates were high enough to sustain the measured concentrations and estimated turnover of DMS, even if the conversion efficiency of DMSPd into DMS was only 10%. DMSPd turnover was significantly correlated with bacterial production (as measured by H-3-thymidine incorporation) and we estimate that DMSPd turnover contributed a mean of 3.4% of the carbon and similar to 100% of the sulfur required for bacterial growth in Gulf of Mexico surface waters. In addition to its role as a precursor of DMS, DMSP deserves attention as an important substrate for bacterioplankton in the euphotic zone.

Kopecky, A. L. and K. H. Dunton (2006). "Variability in drift macroalgal abundance in relation to biotic and abiotic factors in two seagrass dominated estuaries in the western Gulf of Mexico." Estuaries and Coasts **29**(4): 617-629.

We examined the spatial and temporal variability in drift macroalgal abundance in two seagrass dominated estuarine systems on the Texas coast: Redfish Bay (in the Copano-Aransas Estuary) and Lower Laguna Madre. Measurements of benthic macroalgal variability were made in conjunction with a suite of biotic (seagrass biomass, percent cover, blade width and length, shoot density, epiphyte biomass, seagrass blade C:N ratios, and drift macroalgal abundance and composition) and abiotic (inorganic nitrogen and phosphorus concentrations, chlorophyll a, total suspended solids, light attenuation, salinity, temperature, total organic carbon and porewater NH₄⁺) indicators. All parameters were measured at 30 sites within each estuary semiannually from July 2002 to February 2004. Principal components analysis (PCA) was used to examine relationships between drift macroalgal abundance and biotic and abiotic parameters. In both Redfish Bay and Lower Laguna Madre, drift macroalgal distribution was widespread, and during three of four sampling periods, abundance was equal to aboveground biomass of *Thalassia testudinum*, the dominant seagrass. Drift macroalgal abundance was highly variable within sites, between sites, and between seasons in both estuaries. No significant differences in drift macroalgal

abundance were found between Redfish Bay and Lower Laguna Madre. In Redfish Bay, drift macroalgae ($90.1 \pm 10.2 \text{ g m}^{-2}$) tended to accumulate in bare patches within seagrass beds. In Lower Laguna Madre, drift macroalgae ($72.7 \pm 10.7 \text{ g m}^{-2}$) tended to accumulate in areas of dense seagrass cover rather than in bare areas. We found no relationship between drift macroalgal abundance and low ($< 2 \mu\text{M}$) water column nutrient concentrations, and although several of our measured parameters were related to drift macroalgal abundance, none alone sufficiently explained the variability in abundance noted between the two estuarine systems. The contrasting patterns of macroalgal accumulation between Redfish Bay and Lower Laguna Madre likely reflect differences in water circulation characteristics between the two regions as dictated by local physiography, including the shape and orientation of the lagoons, with seasonal variations in macroalgal abundance related to changes in freshwater inflow and nutrient loading.

Krug, E. C. and K. Merrifield (2007). "Marine modification of terrestrial influences on Gulf hypoxia: Part II." Hydrology and Earth System Sciences **11**(1): 191-209.

This study examines potential marine modification of two classes of terrestrial influence on Gulf hypoxia: (1) the flow of nutrient-rich water from the Mississippi/Atchafalaya River Basin and (2) the massive physical, hydrological, chemical and biological change associated with the Atchafalaya's partial capture of the Mississippi River. The latter involves repartitioning of a total flow of about $20\,000 \text{ m}^3 \text{ sec}^{-1}$, equal to that of 13 Nile Rivers, and a sediment load of 210 million metric tonnes yr^{-1} , nearly 20 times that delivered by all of the rivers of the East Coast of the USA. Also involved is the loss of hundreds-to-thousands of years of stored nutrients and organic matter to the Gulf from enormous coastal wetland loss. This study found that the oceanography of the Gulf minimises the impact of both classes of terrestrial influence from the Mississippi River and its nearby estuaries on Gulf hypoxia. Oceanographic conditions give events associated with the Atchafalaya River a disproportionately large influence on Gulf hypoxia. A truly holistic environmental approach which includes the full effects of this highly dynamic coastal area is recommended to better understand and control Gulf hypoxia.

Kvenvolden, K. A. (1995). "A review of the geochemistry of methane in natural gas hydrate." Organic Geochemistry **23**(11-12): 997-1008.

The largest accumulations on Earth of natural gas are in the form of gas hydrate, found mainly offshore in outer continental margin sediment and, to a lesser extent, in polar regions commonly associated with permafrost. Measurements of hydrocarbon gas compositions and of carbon-isotopic compositions of methane from natural gas hydrate samples, collected in subaquatic settings from around the world, suggest that methane guest molecules in the water clathrate structures are mainly derived by the microbial reduction of CO_2 from Sedimentary organic matter. Typically, these hydrocarbon gases are composed of $>99\%$ methane, with carbon-isotopic compositions ($\delta^{13}\text{C(PDB)}$) ranging from -57 to -73 parts per thousand. In only two regions, the Gulf of Mexico and the Caspian Sea,

has mainly thermogenic methane been found in gas hydrate. There, hydrocarbon gases have methane contents ranging from 21 to 97%, with $\delta(13)C$ values ranging from -29 to -57 parts per thousand. At a few locations, where the gas hydrate contains a mixture of microbial and thermal methane, microbial methane is always dominant. Continental: gas hydrate, identified in Alaska and Russia, also has hydrocarbon gases composed of >99% methane, with carbon-isotopic compositions ranging from -41 to -49 parts per thousand. These gas hydrate deposits also contain a mixture of microbial and thermal methane, with thermal methane likely to be dominant. Published by Elsevier Science Ltd

Kvenvolden, K. A. and B. W. Rogers (2005). "Gaia's breath - global methane exhalations." Marine and Petroleum Geology **22**(4): 579-590.

Methane (CH₄) is the most abundant organic compound in the Earth's atmosphere, where it acts as a greenhouse gas and thus has implications for global climate change. The current atmospheric CH₄ budget, however, does not take into account geologically-sourced CH₄ seepage. Geological sources of CH₄ include natural macro- and micro-seeps, mud volcanoes, and other miscellaneous sources such as gas hydrates, magmatic volcanoes, geothermal regions, and mid-ocean ridges. Macro-seeps contribute similar to 25 Tg (teragrams) CH₄/yr to the atmosphere, whereas, micro-seepage contributes perhaps 7 Tg CH₄/yr. Mud volcanoes emit similar to 5 Tg CH₄/yr, and miscellaneous sources emit similar to 8 Tg CH₄/yr to the atmosphere. Thus, the total contribution to the atmosphere from geological sources is estimated to be 45 Tg CH₄/yr, which is significant to the atmospheric organic carbon cycle and should be included in any global inventory of atmospheric CH₄. We argue that the atmospheric CH₄ global inventory of the Interplanetary Panel on Climate Change must be adjusted in order to incorporate geologically-sourced CH₄ from naturally occurring seepage. Published by Elsevier Ltd.

Lambert, W. J., P. Aharon, et al. (2008). "Catastrophic hurricane history revealed by organic geochemical proxies in coastal lake sediments: a case study of Lake Shelby, Alabama (USA)." Journal of Paleolimnology **39**(1): 117-131.

We developed a new method for reconstructing millennia-long hurricane records from coastal environments that uses Organic Geochemical Proxies (OGPs) of organic carbon and nitrogen concentrations and their $\delta C-13$ and $\delta N-15$ compositions. The new method is independent of presence/absence of sand layers and improves significantly the severe-storm history resolution. The subject of this investigation is a 1.5 m long sediment core raised at 2.8 m water depth from the center of Lake Shelby, Alabama, a freshwater lake located approximately 250 m from the Gulf of Mexico, from which an overwash sand-layer based record was previously derived. The core contains two distinct sediment units; an upper 62 cm thick, fine-grained, organic-rich lacustrine sapropel (gyttja) that shows no visible structures except one sand lamina at 23.7 cm depth, and an underlying 90 cm thick, organic-poor lagoon/estuary clay unit. The sapropel unit was deposited over a 682 +/- 30 cal year time interval (1320-2002 A.D.) with a mean sedimentation rate of 0.79 +/- 0.04 mm/year. Lake

Shelby's water column exhibits two contrasting states based on water chemistry surveys (i) an "isolated", stratified, mode under calm weather conditions with a relatively low trophic state, and (ii) a "flooded" mode occurring during storm surges when nutrient-rich seawater floods the lake. Statistically significant delta C-13 and delta N-15 positive excursions in organic matter, up to maximum values of -25 (parts per thousand PDB) and 4 (parts per thousand Air N-2), respectively, are interpreted as geochemical responses to the marine intrusions that fertilize the lake, increase light availability, and cause eutrophication spikes. Detailed OGP analyses crossing a sand layer that offers visual evidence of a catastrophic hurricane overwash event at 1717 A.D. exhibit large delta C-13 and delta N-15 positive shifts bounded by rapid returns to base values, thus confirming the validity of the hurricane identification by the OGPs model. Our data indicate that 11 catastrophic hurricanes hit the Alabama coast over the past 682 years with a rough recurrence interval of one in 62 years.

Land, L. S., L. E. Mack, et al. (1997). "Burial diagenesis of argillaceous sediment, south Texas Gulf of Mexico sedimentary basin: A reexamination." Geological Society of America Bulletin **109**(1): 2-15.

Cuttings from a well through a thick section of Miocene-Oligocene mudrocks from Kenedy County, Texas, spanning a depth range of 2130 to 5490 m (7000 to 18 000 ft), have been studied petrographically and geochemically. On the basis of whole-rock chemical analyses, the deepest samples have lost approximate to 18 wt% (and approximately vol%), mostly as CaCO₃, mineral-bound H₂O, and SiO₂, but including additional Ca, as well as Sr, light rare earth elements (REE) (La, Ce, Nd, Sm), Fe, and Li. K₂O and Rb have been added to the deeper rocks. The large chemical changes are accompanied mineralogically by loss of detrital calcite, kaolinite, K-feldspar, Ca-plagioclase, and muscovite, gain of chlorite and albite, and continued reaction of smectitic illite/smectite (I/S) to more illitic (and K-rich) compositions throughout the entire depth interval of the well. The large chemical changes in this thick mud-rich interval almost certainly require advection of water (free convection?) to accomplish the mass transfer. Initial variation in sediment composition is ruled out as a cause of the observed compositional changes with increasing depth because (1) a variety of "immobile" elements (Al₂O₃, TiO₂, Zr, Hf, heavy REE [Er, Yb], Th, and Sc) remain constant relative to each other despite their uneven distribution across various particle size fractions in the sediments; (2) deep Frio shales are unlike Quaternary Gulf of Mexico sediments or average shales; and (3) unreasonable primary mineralogic compositions would be necessary to explain the chemical composition of the deep samples. These results indicate that burial diagenesis of argillaceous sediment can be a considerably more open chemical process than is conventionally assumed, that it can account for the two major chemical cements (calcite and quartz) in associated sandstones, and that it mirrors secular changes in shales throughout geologic time.

Larkin, J., P. Aharon, et al. (1994). "BEGGIATOIA IN MICROBIAL MATS AT HYDROCARBON VENTS IN THE GULF-OF-MEXICO AND

WARM-MINERAL-SPRINGS, FLORIDA." Geo-Marine Letters **14**(2-3): 97-103.

Microbial mats were collected from a variety of sites near hydrocarbon vents along the slope in the northern Gulf of Mexico and, for comparison, from Warm Mineral Springs, Florida, USA. A predominant microorganism in each of the mats was the giant bacterium, *Beggiatoa*. Diameters of the bacterial filaments ranged from about 6 μm to approximately 200 μm . The latter organisms are the largest prokaryotic organisms yet found. All filaments over about 10 μm in diameter contained a large central vacuole, producing a cell with the cytoplasm as a cylindrical tube underlying the cytoplasmic membrane. Sulfur globules were confined to this peripheral layer. Push cores often contained pyrite tubules whose appearance is suggestive of a *Beggiatoa* origin. Determinations of $\delta^{13}\text{C}$ in *Beggiatoa* mats from vents along the Louisiana slope yielded values in the range of -26.6 to -27.9 parts per thousand (PDB), suggesting an unusually high degree of isotope fractionation (-24.9 parts per thousand) relative to the carbon source in the ambient seawater, which is typical of sulfur-oxidizing chemoautotrophs. The presence of S⁰ (elemental sulfur) within cells of *Beggiatoa* resulting from oxidation of H₂S supports the importance of bacterial sulfate reduction processes in the underlying vents for the sustenance of the *Beggiatoa* mats.

Larkin, J. M. and M. C. Henk (1996). "Filamentous sulfide-oxidizing bacteria at hydrocarbon seeps of the Gulf of Mexico." Microscopy Research and Technique **33**(1): 23-31.

Mats consisting of the large sulfide-oxidizing bacterium, *Beggiatoa*, were collected from the sediment/water interface at several locations in the Gulf of Mexico. The collection sites were associated with the presence of petroleum hydrocarbons or the microbial breakdown products of the hydrocarbons. The morphologies of the mats varied with the nature of the underlying sediments, and some mats were pigmented either yellow or orange instead of the usual white. At one site, *Beggiatoa* were found that had a diameter of nearly 200 μm , making them the largest prokaryotic organism known. In filaments with a diameter of over approximately 10 μm the cytoplasm was restricted to a thin layer immediately underlying the cell membrane, and the majority of the cell consisted of a vacuole with unknown contents. *Beggiatoa* filaments often rotated as they moved by gliding. Parallel rows of 15 nm diameter pores were found on the surface of the *Beggiatoa*s. The pores may have been wound in a spiral fashion around the cell. These pores may be involved in the gliding motility of the bacteria by the motion imparted by the excretion of slime through the pores. Several structures with the typical morphology of prokaryotic cells but lacking a cell wall were found within the vacuolar and cytoplasmic portions of the hollow *Beggiatoa*s. Some of these internal "symbionts" ultrastructurally resembled methanotrophic bacteria like those that have been seen in animals taken from vent areas. Other symbionts ultrastructurally resembled autotrophic bacteria with carboxysome-like structures. These internal symbionts may enable the *Beggiatoa* to grow in different environments on different carbon sources. They also provide important evidence for the endosymbiotic theory of the evolution of internal organelles of eukaryotic organisms. (C) 1996 Wiley-Liss, Inc.

Lee, R. W. and J. J. Childress (1995). "ASSIMILATION OF INORGANIC NITROGEN BY SEEP MYTILID IA, AN UNDESCRIBED DEEP-SEA MUSSEL CONTAINING METHANOTROPHIC ENDOSYMBIONTS - FATE OF ASSIMILATED NITROGEN AND THE RELATION BETWEEN METHANE AND NITROGEN ASSIMILATION." Marine Ecology-Progress Series **123**(1-3): 137-148.

Undescribed deep-sea mussels containing methanotrophic endosymbionts (seep mytilid Ia) are found at high densities around hydrocarbon seeps of the Gulf of Mexico where methane, nitrate and ammonium are present at high concentrations. In this study we investigated assimilation of ammonium, nitrate, glycine and methane using N-15- and C-13-labelled tracers to determine sites of assimilation, rates of assimilation, and the chemical form in which assimilated C and N appears. We then investigated the interaction between inorganic nitrogen assimilation and methane assimilation to assess whether they are directly dependent on each other. (NO₃-)-N-15, (NH₃)-N-15 and (CH₄)-C-13 were assimilated primarily into the gills where the bacteria are located, with negligible incorporation into symbiont-free tissue. In contrast, (CN)-C-13-N-15-glycine was assimilated equally into gill and symbiont-free tissue. These results indicate that inorganic N is assimilated in the gill tissue. The bulk of C-13 and N-15 label from methane and ammonium incubations was in the 80% EtOH soluble fraction, suggesting that the primary assimilation product was low-molecular-weight metabolites. Some C-13 was incorporated into carbon storage products. Mussels that assimilated excess (CH₄)-C-13 converted 35% of (CH₄)-C-13 into an EtOH insoluble form. Negligible N-15 label was observed in this fraction. Inorganic N assimilation and methane assimilation were not tightly coupled. N assimilation was not affected by absence of methane or inhibition of methanotrophy. Methane assimilation was not stimulated by increased N assimilation. Seep mytilids were capable of luxury consumption of inorganic N, i.e. C/N assimilation ratios below the average C/N ratio of mussel tissues (4.2). We believe that luxury consumption is supported by C reserves resulting in part from methanotrophy. From relations between CH₄ and N source concentration and assimilation rate, we estimated the environmental conditions that result in balanced C/N assimilation. From this analysis we predict that at environmentally realistic methane and inorganic N concentrations seep mytilids assimilate excess CH₄.

Leonard, J. and R. Deldelumyea (1994). "ELEMENTAL CARBON CONCENTRATION IN THE AIR AROUND TAMPA BAY, FLORIDA, 1990-1991." Journal of the Air & Waste Management Association **44**(6): 804-806.

Elemental carbon (EC) particles have been found in the lungs of dolphins. The question arose as to whether these particles originated over land or water. This project determined the amount of EC particulate found in terrestrial air. Portions of particulate filters and associated data collected during the period from January 1990 through December 1991 were provided by the Florida Department of Environmental Regulation. Using reflectance spectroscopy and laboratory-generated standards, atmospheric concentrations of EC and TSP were determined. This paper addresses the data from those counties which

surround Tampa Bay. In the spring of 1992, a television news station reported that researchers at Mote Marine Institute had found black carbon particulates in the lungs of dolphins (reported as "...dolphins with Black Lung Disease..."). The dolphins were found in the Gulf of Mexico off the coast of Florida.¹ In discussions with a principal investigator of the dolphin study, the question arose as to whether these particulates came from urban or marine sources. No comprehensive investigation of soot concentrations in the air over Florida had been made. This study reports the elemental carbon (EC) content of urban particulate matter in the Tampa Bay region, where the affected dolphins were discovered between 1988 and 1990 (Sarasota County). This is the first step toward answering whether urban concentrations of EC were sufficient to contribute measurably to the EC found in the marine environment. Future efforts will address marine concentrations and sources of EC. Elemental carbon, commonly termed "soot," is a product of incomplete combustion. Common urban sources of EC in particulate matter include both mobile sources (diesel-powered buses, cars, and trucks) and point sources (incinerators, power plants and home heating units). The State of Florida operates environmental monitoring stations in selected municipalities around the state. At these stations, which were sited according to EPA requirements², Total Suspended Particulate (TSP) samples were collected using the accepted methods.³ These samples were suitable for EC analysis. Samples collected in the Tampa Bay region in 1990 and 1991 were analyzed for EC content using reflectance spectroscopy. EC concentrations were calculated in micrograms per cubic meter ($\mu\text{g}/\text{m}^3$).

Levin, L. A. (2005). Ecology of cold seep sediments: Interactions of fauna with flow, chemistry and microbes. Oceanography and Marine Biology - an Annual Review, Vol. **43**. **43**: 1-46.

Cold seeps occur in geologically active and passive continental margins, where pore waters enriched in methane are forced upward through the sediments by pressure gradients. The advective supply of methane leads to dense microbial communities with high metabolic rates. Anaerobic methane oxidation presumably coupled to sulphate reduction facilitates formation of carbonates and, in many places, generates extremely high concentrations of hydrogen sulphide in pore waters. Increased food supply, availability of hard substratum and high concentrations of methane and sulphide supplied to free-living and symbiotic bacteria provide the basis for the complex ecosystems found at these sites. This review examines the structures of animal communities in seep sediments and how they are shaped by hydrologic, geochemical and microbial processes. The full size range of biota is addressed but emphasis is on the mid-size sediment-dwelling infauna (foraminiferans, metazoan meiofauna and macrofauna), which have received less attention than megafauna or microbes. Megafaunal biomass at seeps, which far exceeds that of surrounding non-seep sediments, is dominated by bivalves (mytilids, vesicomysids, lucinids and thyasirids) and vestimentiferan tube worms, with pogonophorans, cladorhizid sponges, gastropods and shrimp sometimes abundant. In contrast, seep sediments at shelf and upper slope depths have infaunal densities that often

differ very little from those in ambient sediments. At greater depths, seep infauna exhibit enhanced densities, modified composition and reduced diversity relative to background sediments. Dorvilleid, hesionid and ampharetid polychaetes, nematodes, and calcareous foraminiferans are dominant. There is extensive spatial heterogeneity of microbes and higher organisms at seeps. Specialized infaunal communities are associated with different seep habitats (microbial mats, clam beds, mussel beds and tube worms aggregations) and with different vertical zones in the sediment. Whereas fluid flow and associated porewater properties, in particular sulphide concentration, appear to regulate the distribution, physiological adaptations and sometimes behaviour of many seep biota, sometimes the reverse is true. Animal-microbe interactions at seeps are complex and involve symbioses, heterotrophic nutrition, geochemical feedbacks and habitat structure. Nutrition of seep fauna varies, with thiotrophic and methanotrophic symbiotic bacteria fueling most of the megafaunal forms but macrofauna and most meiofauna are mainly heterotrophic. Macrofaunal food sources are largely photosynthesis-based at shallower seeps but reflect carbon fixation by chemosynthesis and considerable incorporation of methane-derived C at deeper seeps. Export of seep carbon appears to be highly localized based on limited studies in the Gulf of Mexico. Seep ecosystems remain one of the ocean's true frontiers. Seep sediments represent some of the most extreme marine conditions and offer unbounded opportunities for discovery in the realms of animal-microbe-geochemical interactions, physiology, trophic ecology, biogeography, systematics and evolution.

Lin, S. and J. W. Morse (1991). "SULFATE REDUCTION AND IRON SULFIDE MINERAL FORMATION IN GULF OF MEXICO ANOXIC SEDIMENTS." American Journal of Science **291**(1): 55-89.

Sulfate reduction and iron sulfide mineral formation were investigated in Mississippi River delta and Gulf of Mexico continental shelf and slope sediments. Sulfate reduction rates and pyrite concentrations generally decrease exponentially with increasing overlying water depth. This is probably a result of decreasing sedimentation rates and organic carbon concentrations with increasing water depth. A linear relationship between sulfate reduction rates and organic carbon concentrations as well as normal marine C/S ratios indicate that organic carbon is probably limiting sulfate reduction and iron sulfide mineral formation in this region. Organic carbon reactivity appears to be substantially higher in Mississippi River delta sediments than in other sediments from this region. Mississippi River delta and Texas-Louisiana continental shelf sediments are the primary pyrite burial environments. Of the total pyrite deposition in the study area (approximately 6×10^{11} g y⁻¹), about 81 percent is deposited in Texas-Louisiana continental shelf sediments and about 15 percent in Mississippi River delta sediments. The remaining 4 percent is deposited in sediments on the continental slope and the western and southern continental shelf areas.

Liu, H. B., M. J. Dagg, et al. (2005). "Mesozooplankton consumption of microplankton in the Mississippi River plume, with special emphasis on planktonic ciliates." Marine

Ecology-Progress Series 286: 133-144.

Grazing of mesozooplankton on phytoplankton, ciliates and other microplankton in the Mississippi River plume was studied by on-deck zooplankton addition incubations during March 2002. Diatoms, numerically predominated by the pennate diatom *Pseudonitzschia pseudodelicatissima*, were the most abundant microplankton in the plume. We observed that large cells of all types dominated the mesozooplankton diet and that phytoplankton generally comprised the largest dietary component. Microzooplankton contributed between 2 and 60% to the mesozooplankton diet. At the near-field station (nearest the discharge point of the river), *P. pseudodelicatissimi* concentration was low and consumption of diatoms, ciliates and dinoflagellates by mesozooplankton reflected available concentrations. In the mid-field stations, *P. pseudodelicatissimi* attained very high concentrations (17 000 cells ml⁻¹) but comprised only a small portion of the mesozooplankton diet, which was instead dominated by ciliates and dinoflagellates. At the far-field station (approximately 60 km distance from the discharge point), *P. pseudodelicatissimi* concentration was intermediate but mesozooplankton clearance rates were still higher on ciliates and dinoflagellates at these stations. This pattern may have been established by changes in the composition of the mesozooplankton grazer community, by the inability of some mesozooplankton to efficiently ingest the long (>100 μm) and large-sized diatoms, or by the production of toxins by *P. pseudodelicatissimi* that prevent it from being grazed by mesozooplankton. Our findings are consistent with an earlier published conceptual model in that (1) the abundance of microzooplankton (ciliates) was high in the near- to mid-field and then decreased toward the far-field, in parallel with phytoplankton stock; (2) mesozooplankton consumed large rather than small prey, thereby affecting the structure of the phytoplankton and microzooplankton community; (3) phytoplankton, dominated by diatoms, were the major food source for mesozooplankton in the plume.

Liu, X. W., Z. H. A. Wang, et al. (2006). "Spectrophotometric measurements of pH in-situ: Laboratory and field evaluations of instrumental performance." Environmental Science & Technology **40**(16): 5036-5044.

Automated in-situ instrumentation has been developed for precise and accurate measurements of a variety of analytes in natural waters. In this work we describe the use of 'SEAS' (spectrophotometric elemental analysis system) instrumentation for measurements of solution pH. SEAS-pH incorporates a CCD-based spectrophotometer, an incandescent light source, and dual pumps for mixing natural water samples with a sulfonephthalein indicator. The SEAS-pH optical cell consists of either a liquid core waveguide (LCW, Teflon AF-2400) or a custom-made PEEK cell. Long optical path lengths allow use of indicators at low concentrations, thereby precluding large indicator-induced pH perturbations. Laboratory experiments show that pH measurements obtained using LCW and PEEK optical cells are indistinguishable from measurements obtained using conventional spectrophotometric cells and high-performance spectrophotometers. Deployments in the Equatorial Pacific and the Gulf of Mexico demonstrate that SEAS-pH instruments are capable of obtaining vertical

pH profiles with high spatial resolution. SEAS-pH deployments at a fixed river-site (Hillsborough River, FL) demonstrate the capability of SEAS for observations of diel pH cycles with high temporal resolution. The in-situ precision of SEAS-pH is assessed as 0.0014 pH units, and the system's measurement frequency is approximately 0.5 Hz. This work indicates that in-situ instrumentation can be used to provide accurate, precise, and highly resolved observations of carbon-system transformations in the natural environment.

Livingston, R. J., S. E. McGlynn, et al. (1998). "Factors controlling seagrass growth in a gulf coastal system: Water and sediment quality and light." *Aquatic Botany* **60**(2): 135-159.

A combined field descriptive/experimental and laboratory experimental study was carried out to determine the relationships of water quality, qualitative and quantitative light factors and sediment characteristics in the definition of the distribution of submerged aquatic vegetation (SAV) offshore of two streams, one polluted and one natural, that drain into the northeastern Gulf of Mexico. Release of pulp mill effluents into a small drainage system were associated with increased loading of dissolved organic carbon (DOC), water color and nutrients to offshore areas relative to an unpolluted reference system. This loading resulted in changes of water quality factors and light transmission characteristics in the receiving Gulf area. Sediments in affected offshore areas were characterized by increased silt/clay fractions and altered particle size relative to reference sites. Based on the field data, the best (statistically significant) predictors of SAV distribution were photic depths, qualitative aspects of wave length distributions, water quality factors (color, DOC and chlorophyll a) and sediment characteristics. Photic depth?, were good predictors of SAV distribution, with depth as an important modifying factor. Mesocosm experiments showed that pulp mill effluent in direct contact with *Thalassia testudinum* and *Syringodium filiforme* had significant adverse impacts on growth at relatively low concentrations (1-2%) of effluent. Light mesocosm experiments indicated that light levels in inshore Fenholloway areas were associated with reduced growth of *Halodule wrightii*, *S. filiforme* and *T. testudinum*. Field transfer experiments showed that altered sediment and water quality in inshore polluted areas induced significant adverse effects on growth indices of all three species. By comparing the field and experimental results, a hierarchy of habitat requirements for the subject seagrass species was determined. Salinity, temperature and depth restraints are important habitat variables that control seagrass growth; when such variables are not limiting, light, sediment and nutrient characteristics become important in the determination of the distribution of seagrasses in coastal areas. (C) 1998 Elsevier Science B.V.

Lohrenz, S. E. and W. J. Cai (2006). "Satellite ocean color assessment of air-sea fluxes of CO₂ in a river-dominated coastal margin." *Geophysical Research Letters* **33**(1). 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. We describe an algorithm for assessment of surface water partial

pressure of CO₂ (pCO₂) from MODIS imagery in the northern Gulf of Mexico. Principal component analysis and multiple regression were used to relate surface pCO₂ to environmental variables (T, S, chlorophyll). Subsequent retrieval of corresponding products from MODIS-Aqua L1B data permitted the assessment of regional distributions of pCO₂. An area of low pCO₂ was evident in the vicinity of the Mississippi River delta, consistent with field observations. Regional surface air to sea fluxes of CO₂ were estimated as 2.0-4.2 mmol C m⁻² d⁻¹.

Lohrenz, S. E., G. L. Fahnenstiel, et al. (1994). "SPATIAL AND TEMPORAL VARIATIONS OF PHOTOSYNTHETIC PARAMETERS IN RELATION TO ENVIRONMENTAL-CONDITIONS IN COASTAL WATERS OF THE NORTHERN GULF-OF-MEXICO." *Estuaries* **17**(4): 779-795.

On a series of eight cruises conducted in the northern Gulf of Mexico, efforts were made to characterize temporal and spatial variability in parameters of the photosynthesis-irradiance saturation curve (P-max(B), alpha(B), I-k) and to relate the observed variations to environmental conditions. Experiments to examine the importance of diel variation in upper mixed layer populations were conducted in July-August 1990 and March 1991. During July-August 1990, P-max(B) and I-k showed significant increases and alpha(B) decreased during the photoperiod in both river plume and shelf-slope populations. During March 1991, no consistent covariance of P-I parameters with local time was found, although highest values of alpha(B) in the river plume were observed in early morning. Seasonal variation in P-max(B), and alpha(B) were correlated with temperature. Spatial variations of photosynthetic parameters in the upper mixed layer ranged from twofold to threefold within any given cruise. Variations of photosynthetic parameters in the upper mixed layer were related to principal components derived from environmental variables, including temperature, salinity, nutrients, mixed layer depth, attenuation coefficient, and daily photosynthetically available radiation (PAR). Greater than 70% of the variation in the environmental variables could be accounted for by two principal components; the majority of this variation was associated with the first principal component, which was generally strongly correlated with salinity, nutrients, mixed layer depth, and attenuation coefficient. Correlations of P-max(B), alpha(B), and I-k with the first principal component were found to be significant in some cases, an indication that spatial variability in P-I parameters was related to river outflow. Variation of P-I parameters in relation to depth and PAR were evaluated by regressions with principal components derived from depth, temperature, and mean daily PAR. For most cruises, P-max(B), and I-k were negatively correlated with the first principal component, which was strongly positively correlated with depth and negatively correlated with daily PAR. This was consistent with a decrease in both P-max(B), and I-k with depth that could be related to decreasing daily PAR. Positive correlations of alpha(B) with the first principal component for two cruises, March 1991 and April 1992, indicated an increasing trend with depth. In conclusion, relationships between P-I parameters and environmental variables in the region of study were significant in some cases, but variation between cruises made it difficult to generalize. We attributed this variation to the physically dynamic characteristics

of the region and the possible effects of variables that were not included in the analysis such as species composition. Our findings do support the view that a limited set of observations may be adequate to characterize P-I parameter distributions in a given region within a restricted period of time.

Lohrenz, S. E., G. L. Fahnenstiel, et al. (1997). "Variations in primary production of northern Gulf of Mexico continental shelf waters linked to nutrient inputs from the Mississippi River." Marine Ecology-Progress Series **155**: 45-54.

Increases in nutrient concentrations in the Mississippi River over the past 35 yr have led to speculation that primary production of organic carbon has been elevated as a result of increased nutrient fluxes that have occurred in the northern Gulf of Mexico coastal ecosystem. However, studies thus far have not provided direct demonstration of temporal relationships between measured primary production in continental shelf waters and river-borne nutrient fluxes. This investigation compared temporal variations in primary production with associated annual and interannual changes in river-borne nutrient inputs. Primary production in shelf waters near the river delta were found to be significantly correlated with nitrate (NO₃-) + nitrite (NO₂-) concentrations and fluxes over a 6 yr period from 1988 to 1994. Although light limitation was probably an important factor during winter months, a positive correlation was demonstrated between river inputs of NO₃-+NO₂- and primary production for data collected from other times of the year. Peak nutrient inputs generally occurred in the spring. The magnitude of the riverborne NO₃-+NO₂- inputs averaged 106% of estimated nitrogen requirements for phytoplankton in the river-impacted region, considerably greater than in Amazon shelf waters, which have been less subject to anthropogenic nutrient increases. The possibility exists that further increases in anthropogenic nutrients in the Mississippi River could lead to higher and more widespread primary production, and this may intensify and extend the depletion of oxygen that has already been observed in the Louisiana shelf ecosystem. However, such a prediction is difficult because relationships between increasing nutrient inputs and primary production are unlikely to be Linear, and a complete understanding of processes intermediate between primary production of organic matter and oxygen depletion in bottom waters on the Louisiana shelf is still lacking.

Lopezveneroni, D. and L. A. Cifuentes (1994). "TRANSPORT OF DISSOLVED ORGANIC NITROGEN IN MISSISSIPPI RIVER PLUME AND TEXAS-LOUISIANA CONTINENTAL-SHELF NEAR-SURFACE WATERS." Estuaries **17**(4): 796-808.

Dissolved organic nitrogen (DON) in near-surface (<20 m depth) waters of the Texas-Louisiana continental shelf is the predominant form of total dissolved nitrogen that is advected by the Mississippi-Atchafalaya River plume. Relatively high DON concentrations associated with low-salinity (<33 psu) waters throughout the year can be traced within the plume along the Texas-Louisiana inner shelf. DON concentrations throughout the shelf were significantly higher near the Mississippi-Atchafalaya outflow region relative to downstream inner Gulf shelf locations. Significant intercruise variations were also evident, with the

highest concentrations during May 1998 and lower values in October 1992. At a fixed location off the Mississippi River outflow region DON concentration covaried inversely with salinity on time scales of hours to months, confirming that source water is a determining factor for variations of bulk DON concentrations in the region. Similar variations in upper water DON concentrations at different locations and seasons occurred in both plume and nonplume waters, which resembled the seasonal concentration changes of riverine nitrogen, and show that this pool is useful in tracing the influence of riverine-derived nitrogen on the overall nitrogen balance of the NW Gulf of Mexico's continental shelf. Plume and nonplume DON concentrations deviated from mixing lines between riverine and oceanic endmembers, suggesting that plume waters may be a sink and nonplume waters may be a source of a labile fraction of DON in the region.

Loubere, P. (1997). "Benthic foraminiferal assemblage formation, organic carbon flux and oxygen concentrations on the outer continental shelf and slope." Journal of Foraminiferal Research **27**(2): 93-100.

A model is presented that defines the interaction of benthic foraminiferal shell production and taphonomy over a range of organic carbon flux and bottom water oxygen values. This model applies to outer continental shelf and slope environments where the sediments are hemipelagic mud, there is net sediment accumulation and limited current transport, and sediment column properties are primarily controlled by sea-bed organic carbon flux and bottom water oxygen content. Data on sediment biogeochemistry from the Gulf of Mexico and the central California margin are used to define an organic carbon flux-bottom water oxygen field. Within this field, observations of foraminiferal standing stocks and absolute test abundances indicate that there are four different production-taphonomic regimes. These are: (1) the high organic matter flux (more than 6 to 7 gC/m²/yr)-low bottom water oxygen (less than 1 ml/L) setting where there is heterogeneous shell generation in the sediment column, limited oxic taphonomy and inefficient sediment mixing resulting in highly variable assemblages on small spatial scales; (2) the moderate organic carbon flux (between 2 and 6 gC/m²/yr)-moderate bottom water oxygen (between 1.5 and 3 ml/L) setting where there is heterogeneous shell production in the sediment column, oxic taphonomy in the top 5 cm of sediments and efficient sediment mixing; (3) the moderate organic carbon flux-high bottom water oxygen (greater than 3.5 ml/L) setting where there are vertically stratified microhabitats, a distinct taphonomic zone in the upper 3 to 4 cm of the sediments, significant infaunal shell generation below the taphonomic zone and sediment mixing that cannot blend completely across that zone; and (4) the low organic carbon flux-high bottom water oxygen setting where shell production is close to the sediment-water interface, taphonomy occurs in the upper 1 to 2 cm of the sediments and effective mixing reaches to sediment depths of 5 to 8 cm. The microhabitats available to the foraminifera and the changes in the taphonomic-sediment mixing regime within these settings can help explain the significant fossil assemblage composition differences across the organic carbon flux-bottom water oxygen field that are reported in the literature.

Loubere, P., A. Gary, et al. (1993). "SEA-BED BIOGEOCHEMISTRY AND BENTHIC FORAMINIFERAL BATHYMETRIC ZONATION ON THE SLOPE OF THE NORTHWEST GULF-OF-MEXICO." Palaios **8**(5): 439-449.

The bathymetric zonation of benthic Foraminiferal taxa in the northwest Gulf of Mexico is summarized and compared to several important environmental parameters measured in boxcores collected along a depth transect. The parameters are bottom water temperature, organic carbon flux, bottom water oxygen content, biogeochemical gradients within the sediments and sedimentation regime. The prominent Foraminiferal boundary between 170 and 200 m is associated with the position of the mud-line in the northwest Gulf. Below this, assemblage changes are more gradational with water depth and, between 200 and 600 m, appear to be related to gradients in temperature, oxygen supply and organic carbon flux. Between 600 and 2000 m bathymetric zonation correlates to the organic carbon flux profile. An analysis of sediment pore water geochemistry and sedimentary features in the box-cores shows that there is a progressive change in the vertical distribution and character of potential microhabitats within the sediments down the slope of the northwest Gulf. From 250 to about 700 m water depth the biogenic structures observed in the sediments are abundant and complex, and the biogeochemical gradients in the sediments are steep. The visible complexity and chemical gradients gradually decrease with increasing water depth so that by 1000 m the anoxic boundary is deeper than 7 cm in our boxcores. At water depths greater than 1200 m the sediments are homogeneous, oxidized, hemipelagites. The published Foraminiferal bathymetric zonation of the N.W. Gulf appears to follow this gradient in sedimentary environments which must influence the generation of benthic Foraminiferal assemblages. The gradient is largely controlled by the organic carbon flux to the sea-bed.

Luczkovich, J. J., G. P. Ward, et al. (2002). "Determining the trophic guilds of fishes and macroinvertebrates in a seagrass food web." Estuaries **25**(6A): 1143-1163.

We established trophic guilds of macroinvertebrate and fish taxa using correspondence analysis and a hierarchical clustering strategy for a seagrass food web in winter in the northeastern Gulf of Mexico. To create the diet matrix, we characterized the trophic linkages of macroinvertebrate and fish taxa present in *Halodule wrightii* seagrass habitat areas within the St. Marks National Wildlife Refuge (Florida) using binary data, combining dietary links obtained from relevant literature for macroinvertebrates with stomach analysis of common fishes collected during January and February of 1994. Hierarchical average-linkage cluster analysis of the 73 taxa of fishes and macroinvertebrates in the diet matrix yielded 14 clusters with diet similarity greater than or equal to 0.60. We then used correspondence analysis with three factors to jointly plot the coordinates of the consumers (identified by cluster membership) and of the 33 food sources. Correspondence analysis served as a visualization tool for assigning each taxon to one of eight trophic guilds: herbivores, detritivores, suspension feeders, omnivores, molluscivores, meiobenthos consumers,

macrobenthos consumers, and piscivores. These trophic groups, cross-classified with major taxonomic groups, were further used to develop consumer compartments in a network analysis model of carbon flow in this seagrass ecosystem. The method presented here should greatly improve the development of future network models of food webs by providing an objective procedure for aggregating trophic groups.

Lugo-Fernandez, A. and P. F. Roscigno (1999). "Environmental assessment of the impact of ozone to the neuston of the sea-surface microlayer of the Gulf of Mexico." Environmental Monitoring and Assessment **55**(2): 319-346.

Substantial amounts of NO_x (similar to 146 000 t/y) and total hydrocarbons (similar to 294 000 t/y) are released to the marine atmosphere by the large number of oil and gas operations over Federal waters of the Gulf of Mexico (GOM). Under appropriate meteorological conditions these emissions react to form ozone (0-54 $\mu\text{g}/\text{m}^3$ over-water) which can affect the marine environment. Using a dry deposition model, this work examines the amount of ozone derived from oil and gas offshore operations and deposited in the sea surface of the Gulf of Mexico, and assesses its impact on the neuston of the sea-surface microlayer. Surface integrated estimates of ozone deposited from oil and gas operations over the sea surface ranges from 400 kg to 1800 kg which results in sea surface concentrations of similar to 15 $\mu\text{g}/\text{m}^3$. This estimate and the actual toxic ozone levels suggest no acute, toxic impacts to the neuston. However, indirect effects may occur through changes to the pelagic foodwebs and organic carbon pathways. Another potential pathway for ozone impacting the environment is through the production of bromate. Based on the concentrations and time scales (11-139 days) only sublethal effects appear to occur, but uncertainties associated with this assessment need to be further studied. From an ecological perspective, the environmental impacts and risks of NO_x and VOC discharges from offshore platforms need to be assessed for neuston and other components of the marine ecosystem.

Macauley, J. M., V. D. Engle, et al. (1995). "AN ASSESSMENT OF WATER-QUALITY AND PRIMARY PRODUCTIVITY IN PERDIDO BAY, A NORTHERN GULF-OF-MEXICO ESTUARY." Environmental Monitoring and Assessment **36**(3): 191-205.

Perdido Bay is a shallow estuarine system of approximately 130 km² with three major freshwater inputs. On a seasonal basis the productivity and chlorophyll a concentration of phytoplankton in Perdido Bay are controlled by temperature. One input, Eleven Mile Creek, is influenced by a paper mill discharge. Eleven Mile Creek exhibits high levels of light attenuation, high concentrations of dissolved nutrients, and low rates of carbon fixation that are significantly different from the other inputs or areas of Perdido Bay and productivity in Eleven Mile Creek is light limited. Upper Perdido Bay had slightly elevated concentrations of dissolved nutrients which correlate with significantly higher rates of carbon fixation and phytoplankton biomass. Nutrients and color from Eleven Mile Creek are diluted by the Perdido River inflow, restricting nutrient and light limitations to

the area at the mouth of Eleven Mile Creek.

MacAvoy, S. E., R. S. Carney, et al. (2002). "Use of chemosynthetic biomass by large, mobile, benthic predators in the Gulf of Mexico." Marine Ecology-Progress Series **225**: 65-78.

The Gulf of Mexico supports communities of chemoautotrophic and heterotrophic fauna associated with hydrocarbon seeps. The chemoautotrophic invertebrates, mostly dense epifaunal assemblages of mussels and tubeworms, derive their nutrition from symbiotic relationships with sulfide- or methane-oxidizing bacteria. The extent to which benthic predatory fauna feed on the chemoautotrophic assemblages has been an open question. Owing to differences in stable isotope values between chemosynthetic- and photosynthetic-derived biomass, isotopic characterization of predatory fauna would be useful in determining their dependence upon chemoautotrophs for food. Carbon and sulfur stable isotope analyses reveal that fishes with similar feeding strategies (rat tail [*Nezumia* sp.] and eels [*Synaphobranchus* sp., *Ophichthus cruentifer* and *Dysommia rugosa*]) have similar $\delta(13)C$ values (-32.7 and -42.5‰, respectively), reflecting chemoautotrophic carbon. Large vagrant predators/scavengers such as isopods *Bathynomus giganteus*, hagfish *Eptatretus* sp. and spider crabs *Rochina crassa*, have isotope values closer to oceanic ranges ($\delta(13)C$: -20 to -18‰ per thousand; $\delta(34)S$: 18 to 20‰ per thousand), although some individual *Eptatretus* sp. and *R. crassa* show a chemosynthetic component. Colonist invertebrates, such as the sea star (*Sclerasterias* cf. *tanneri*) and a predatory snail *Buccinum canetae*, have greatly depleted $\delta(13)C$ and $\delta(34)S$ values, indicating an almost 100% reliance on seep production. Nitrogen isotope ratios are depleted (-19‰ per thousand) in some seep areas, and *B. canetae* and *Synaphobranchus* sp. reflect the N-15 depletion (-10 and -3‰ per thousand respectively). On a species-specific basis, some mobile benthic predators from the background fauna obtain close to 100% of their nutrition from seep production, indicating that they are residents of the seeps. There is a high degree of movement in and out of the seep habitat by vagrant benthic predators, and although the majority derive most of their nutritional needs from photosynthetic production, the incorporation of chemosynthetic production is substantial.

MacAvoy, S. E., S. A. Macko, et al. (2003). "Links between chemosynthetic production and mobile predators on the Louisiana continental slope: stable carbon isotopes of specific fatty acids." Chemical Geology **201**(3-4): 229-237.

The Gulf of Mexico supports chemoautotrophic communities associated with hydrocarbon seeps. The chemoautotrophic symbiont-containing metazoans are dominated by mussels and tube worms that harbor bacteria which utilize reduced carbon (CH_4) and sulfur (H_2S) compounds as an energy source. In the deep sea, nutritional input from photosynthetic production is scarce, and chemoautotrophic production may be a significant source of nutrients to mobile, benthic predators. Large and significant differences exist between the stable carbon isotope signatures of chemosynthetic and photosynthetic primary production. This isotopic difference makes it possible to determine the

importance of each type of primary production to heterotrophs because heterotrophs incorporate the isotope signature of their food. Here, we examine the carbon isotope signatures of specific fatty acids in heterotrophic predators caught both within and approximately 2 km from known chemosynthetic communities. Heterotroph fatty acid signatures were compared to those observed in chemoautotrophic symbiont-containing fauna in order to evaluate degree of usage. Most organisms had at least a 6 parts per thousand range in their fatty acids. This reflected patterns of de novo synthesis, with essential and precursor fatty acids being C-13 enriched (in heterotrophs) and highly unsaturated fatty acids being C-13 depleted. The fatty acid $\delta(13)C$ values show that heterotrophs had a wide range in their utilization of chemosynthetic production. *Bathynomus giganteus* (giant isopod), captured off-site, did not utilize chemosynthetic production. Its nonessential fatty acids ranged from -26.3 parts per thousand to -18.8 parts per thousand ($\delta(13)C$), reflecting kinetic isotope effects during de novo synthesis. Essential omega-3 fatty acids, which are directly incorporated from diet, originated from photosynthetic production ($\delta(13)C = -16.2$ parts per thousand). *Sclerasterias cf. tanneri* (starfish), captured on-site, relied predominantly on chemosynthetic production. Its fatty acid $\delta(13)C$ values ranged from -30.5 parts per thousand to -42.2 parts per thousand, reflecting chemosynthetic production. Other predators such as *Eptatretus* sp. (hagfish) and *Rochina crassa* (spider crab) derived variable percentages of their fatty acid pool from chemosynthetic production, estimated to be 38% and 5%, respectively. Bulk analysis of $\delta(15)N$ and $\delta(34)S$ show chemosynthetic production usage patterns generally consistent with the specific fatty acid $\delta(13)C$ data. (C) 2003 Elsevier B.V All rights reserved.

MacDonald, I. R., I. Leifer, et al. (2002). "Transfer of hydrocarbons from natural seeps to the water column and atmosphere." *Geofluids* 2(2): 95-107.

Results from surface geochemical prospecting, seismic exploration and satellite remote sensing have documented oil and gas seeps in marine basins around the world. Seeps are a dynamic component of the carbon cycle and can be important indicators for economically significant hydrocarbon deposits. The northern Gulf of Mexico contains hundreds of active seeps that can be studied experimentally with the use of submarines and Remotely Operated Vehicles (ROV).

Hydrocarbon flux through surface sediments profoundly alters benthic ecology and seafloor geology at seeps. In water depths of 500-2000 m, rapid gas flux results in shallow, metastable deposits of gas hydrate, which reduce sediment porosity and affect seepage rates. This paper details the processes that occur during the final, brief transition - as oil and gas escape from the seafloor, rise through the water and dissolve, are consumed by microbial processes, or disperse into the atmosphere. The geology of the upper sediment column determines whether discharge is rapid and episodic, as occurs in mud volcanoes, or more gradual and steady, as occurs where the seep orifice is plugged with gas hydrate. In both cases, seep oil and gas appear to rise through the water in close proximity instead of separating. Chemical alteration of the oil is relatively minor during transit through the water column, but once at the sea surface its more

volatile components rapidly evaporate. Gas bubbles rapidly dissolve as they rise, although observations suggest that oil coatings on the bubbles inhibit dissolution. At the sea surface, the floating oil forms slicks, detectable by remote sensing, whose origins are laterally within similar to 1000 m of the seafloor vent. This contradicts the much larger distance predicted if oil drops rise through a 500 m water column at an expected rate of similar to 0.01 m s^{-1} while subjected to lateral currents of similar to 0.2 m s^{-1} or greater. It indicates that oil rises with the gas bubbles at speeds of similar to 0.15 m s^{-1} all the way to the surface.

Macko, S. A., L. Entzeroth, et al. (1984). "REGIONAL DIFFERENCES IN NITROGEN AND CARBON ISOTOPES ON THE CONTINENTAL-SHELF OF THE GULF OF MEXICO." Naturwissenschaften **71**(7): 374-375.

Malmstrom, R. R., R. P. Kiene, et al. (2004). "Identification and enumeration of bacteria assimilating dimethylsulfoniopropionate (DMSP) in the North Atlantic and Gulf of Mexico." Limnology and Oceanography **49**(2): 597-606.

The algal-derived compound dimethylsulfoniopropionate (DMSP), which is the precursor of the climatically active gas dimethylsulfide, is potentially an important source of carbon and sulfur to marine bacterioplankton. Currently, bacteria of the Roseobacter clade, a subgroup of alpha-proteobacteria, are hypothesized to be the key participants in the metabolism of DMSP. To test this hypothesis, we used a combination of microautoradiography and fluorescence in situ hybridization (Micro-FISH) to identify the bacteria assimilating ^{14}C DMSP in the Gulf of Mexico, the Gulf of Maine, and the Sargasso Sea. On average, half of the bacterial community assimilated DMSP in these environments. Members of the alpha-proteobacteria dominated DMSP assimilation, accounting for 35-40% of bacteria assimilating DMSP. Cytophaga-like bacteria and gamma-proteobacteria each accounted for 15-30% of DMSP-assimilating cells. The alpha-proteobacteria accounted for a greater fraction of the DMSP-assimilating community than expected based on their overall abundance, whereas Cytophaga-like bacteria were typically underrepresented in the DMSP-assimilating community. Members of the Roseobacter clade assimilated more DMSP on a per-cell basis than any other group, but they did not account for most of the DMSP assimilation, nor were they always present even when DMSP turnover was high. These results indicate that the biogeochemical flux of dissolved DMSP is mediated by a large and diverse group of heterotrophic bacteria.

Manickchand-Heileman, S., L. A. Soto, et al. (1998). "A preliminary trophic model of the continental shelf, south-western Gulf of Mexico." Estuarine Coastal and Shelf Science **46**(6): 885-899.

A preliminary mass-balance trophic model was constructed to determine the flow of energy in a community of fish and invertebrates on the continental shelf of the south-western Gulf of Mexico. Input parameters were taken from the literature, except for the biomass of fish groups which was obtained from trawl surveys in the study area. The model consists of 12 fish groups, five invertebrate groups, phytoplankton and detritus. Results indicate an imbalance between primary

production and consumption, with only about 10% of primary production being consumed in the water column. Most of the primary production is exported to detritus which forms the basis of the food-web, with a detritivory/herbivory ratio of 2.5. Benthic invertebrates play a significant role in transferring energy from detritus to higher trophic levels. Eight discrete trophic levels were found, with very reduced flow at levels higher than the fifth. The highest fractional trophic level is 4.3, and consists of sharks. Analysis of mixed trophic impacts showed that detritus and lower trophic levels have a significant positive impact on other groups in the system. Mean transfer efficiency is 9.2%. Some whole system properties are also given. Of net primary production, 6.7% is required to sustain current catch levels, suggesting that the resources in this area are fully exploited. (C) 1998 Academic Press Limited.

Mayer, L. M., L. L. Schick, et al. (2007). "Marine vs. terrigenous organic matter in Louisiana coastal sediments: The uses of bromine : organic carbon ratios." Marine Chemistry **107**(2): 244-254.

Recent data on the sources of organic carbon buried in the ocean have emphasized the probable importance of terrigenous organic matter in burial budgets of deltaic depocenters. The many markers used to assess relative importance of marine vs. terrestrial sources each have ambiguities. We use the ratio of bromine to organic carbon (Br:OC) as a source indicator for organic matter in the Mississippi delta. Progressive increases in bromine concentrations from the river to the slope indicate increasing content of marine-derived organic matter. Quantitative estimates of marine vs. terrigenous organic matter using Br:OC ratios in a two-endmember mixing model are consistent with recent estimates using a combination of three other source markers [Gordon, E.S., Goni, M.A. 2003. Sources and distribution of terrigenous organic matter delivered by the Atchafalaya River to sediments in the northern Gulf of Mexico. *Geochim. Cosmochim. Acta*, 67:2359-2375]. The Br:OC vs. delta C-13 relationship indicates seaward increase in delta C-13 without proportionate incorporation of marine organic matter, consistent with recent arguments that isotopically depleted terrestrial detritus derived from C3 plants is separated from C4-derived terrigenous organic matter during transport. Decreasing Br:OC ratios downcore at many sites that have significant amounts of marine organic matter indicate that the marine organic matter is preferentially lost during burial diagenesis. This preferential loss constrains the contribution of organic matter burial in deltaic environments to global removal of Br. (c) 2007 Elsevier B.V. All rights reserved.

McKee, B. A., R. C. Aller, et al. (2004). "Transport and transformation of dissolved and particulate materials on continental margins influenced by major rivers: benthic boundary layer and seabed processes." Continental Shelf Research **24**(7-8): 899-926.

Within the benthic boundary layer (BBL) and seabed of river-dominated ocean margins (RiOMars), the timing, kinetics and extent of important biogeochemical processes are greatly influenced by large riverine inputs of dissolved and particulate terrestrial materials. An examination of our current state of knowledge reveals that the rates of primary productivity, sediment deposition,

remineralization and burial in these margins are among the highest of all marine systems. Transport and transformation processes within the benthic region of these RiOMar areas are highly variable (temporally and spatially). As a result, measurement and modeling of these processes are very challenging. A more quantitative understanding of these systems will require coordinated interdisciplinary studies that: (a) better define the quantity and composition of riverine inputs; (b) greatly improve our current knowledge of transport and transformation within the BBL of these systems; (c) focus on the sequential timing of physical forcings (riverine discharge, high energy events); (d) develop new nonclassical diagenetic models; (e) further characterize and delineate differences between sub-environments within a RiOMar and between RiOMar "types"; and, (f) provide a better mechanistic understanding of what controls the net retention of terrestrial materials (diagenetic transformation vs. burial) within RiOMar systems. (C) 2004 Published by Elsevier Ltd.

Mead, R. and M. A. Goni (2006). "A lipid molecular marker assessment of sediments from the Northern Gulf of Mexico before and after the passage of Hurricane Lili." Organic Geochemistry **37**(9): 1115-1129.

A characterization study of lipid molecular markers was undertaken to identify the provenance of organic matter in surface sediments from the Louisiana Shelf, west of the Atchafalaya River before and after the passage of Hurricane Lili (a category 2 storm) in October 2002. During both sampling periods, terrestrially derived organic matter, as revealed by long chain n-alkanes, terrestrial aquatic hydrocarbon ratio (TAR(HC)) and R-sitosterol, was a predominant component of the organic matter, supporting earlier studies. A petroleum derived unresolved complex mixture (UCM) was detected at each station during both sampling events and displayed no statistically significant difference between inshore and offshore stations. The absence of any relationship between the UCM and the bulk radiocarbon isotopic compositions suggests that petroleum derived organic matter does not significantly control the ages of the sedimentary organic carbon (> 2000 years). In addition, sterols, linear, mono- and polyunsaturated fatty acids (FAs) from multiple organic matter sources, including diatoms, dinoflagellates and zooplankton, were also detected at each site. These compounds indicated the sources of organic matter for pre- and post-hurricane samples were similar overall. Surface area-normalized concentrations of n-alkanes and bacterially derived FAs for the pre- and post-hurricane sediments were statistically different between events whereas other parameters such as total sterol and FA concentrations were not. (c) 2006 Elsevier Ltd. All rights reserved.

Milkov, A. V. (2004). "Global estimates of hydrate-bound gas in marine sediments: how much is really out there?" Earth-Science Reviews **66**(3-4): 183-197.

It is generally assumed that oceanic gas hydrates contain a huge volume of natural gases, mainly methane. The most widely cited estimate of global hydrate-bound gas is 21×10^{15} m³ of methane at STP (or similar to 10,000 Gt of methane carbon), which is proposed as a "consensus value" from several independent estimations. This large gas hydrate reservoir is further suggested as

an important component of the global carbon cycle and as a future energy source. Here, I present a revised and updated set of well-justified global estimates and discuss how and why they changed over time. It appears that the global estimates of hydrate-bound gas decreased by at least one order of magnitude from 1970s-early 1980s (estimates on the order of 10^{17} - 10^{18} m³) to late 1980s-early 1990s (10^{16} m³) to late 1990s-present (10^{14} - 10^{15} m³). The decrease of estimates is a result of growing knowledge of the distribution and concentration of gas hydrates in marine sediments and ongoing efforts to better constrain the volume of hydrate-bearing sediments and their gas yield. These parameters appear to be relatively well constrained at present through DSDP/ODP drilling and direct measurements of gas concentrations in sediments. The global estimate of hydrate-bound gas that best reflects the current knowledge of submarine gas hydrate is in the range $(1-5) \times 10^{15}$ m³ (similar to 500-2500 Gt of methane carbon). A significantly smaller global gas hydrate inventory implies that the role of gas hydrates in the global carbon cycle may not be as significant as speculated previously. Gas hydrate may be considered a future energy source not because the global volume of hydrate-bound gas is large, but because some individual gas hydrate accumulations may contain significant and concentrated resources that may be profitably recovered in the future. (C) 2003 Elsevier B.V. All rights reserved.

Milkov, A. V. and R. Sassen (2003). "Two-dimensional modeling of gas hydrate decomposition in the northwestern Gulf of Mexico: significance to global change assessment." Global and Planetary Change **36**(1-2): 31-46.

Thinning of the gas hydrate stability zone (GHSZ) in response to bottom water temperature increases and drops in sea level similar to those during Pliocene and Pleistocene time was modeled on two-dimensional (2D) regional scale in the northwestern Gulf of Mexico. A sea level drop of 100 m is unlikely to significantly influence the stability of gas hydrate, especially when coupled with an expected decrease in water temperature. A bottom water temperature increase of 4 C may lead to appreciable (similar to 30%) thinning of the GHSZ. Neither a 100-m drop in sea level nor a 4 C bottom water temperature increase is hypothesized to initiate significant gas flux from decomposition of gas hydrate. Hydrocarbon gases may have been released from decomposed gas hydrate to sediment at a rate considerably lower than the preliminary estimated late Pleistocene-Holocene total gas seepage from a leaky subsurface petroleum system. Potential input of greenhouse gases into the ocean is suggested to be less significant. Several processes such as recrystallization of gas hydrate in the GHSZ, trapping of free gas below the GHSZ, and microbial oxidation of hydrocarbons in sediment by bacteria and archaea contribute to sequestration and destruction of gas from gas hydrate decomposition. Gas hydrate in the Gulf of Mexico is frequently associated with enormous volumes of authigenic carbonate rock, depleted in C-13, that sequesters a large pool of carbon in sediment and perturbs the carbon cycle. These factors appear to significantly decrease the role of hydrate-derived gas in global change. An improved understanding of how the gas hydrate system of the Gulf of Mexico responds to natural variation will contribute to better

assessment of gas hydrate as an agent of global change. (C) 2002 Elsevier Science B.V All rights reserved.

Mitra, S. and T. S. Bianchi (2003). "A preliminary assessment of polycyclic aromatic hydrocarbon distributions in the lower Mississippi River and Gulf of Mexico." Marine Chemistry **82**(3-4): 273-288.

Water samples were collected in the lower Mississippi River and the Gulf of Mexico in April 1999; sites in the river were sampled again in November 1999. Samples were separated into particulate (C-p) and dissolved (C-w) phases using 0.7 μm glass fiber filters. Each phase was analyzed for polycyclic aromatic hydrocarbons (PAHs). Total PAH abundance in river samples was higher in November of 1999 (C-p: 1300-7000 ng gdw(-1); C-w: 77-430 ng l(-1)) than in April 1999 (C-p: 1100-1700 ng gdw(-1), C-w: 12-25 ng l(-1)), despite higher total suspended sediment concentrations in April. Concentration profiles of PAHs in the lower Mississippi River indicate that compositional differences in PAH particle-water distributions were a function of seasonal discharge across the year. For example, higher PAH distribution coefficients in November correspond to a greater degree of combustion-driven processes indicated by black carbon abundance analyzed in the same samples in a complementary study.

Concentrations of three specific PAHs isolated in the Mississippi River and the Gulf of Mexico (anthracene, benzo[a]anthracene, and benzo[g,h,i]perylene) were fit into a mass balance model in an attempt to constrain sources of PAHs into the gulf. This portion of the study was based on a limited number of samples.

However, these preliminary mass balance calculations indicated that in 1999 on an annual scale, fluvial and atmospheric contributions of PAHs to the Gulf of Mexico were relatively negligible (10(0) kg) and that coastal erosion (10(3) kg) may have been the most significant source of PAHs into the gulf. (C) 2003 Elsevier Science B.V. All rights reserved.

Mitra, S., T. S. Bianchi, et al. (2000). "Terrestrially derived dissolved organic matter in the Chesapeake Bay and the Middle Atlantic Bight." Geochimica Et Cosmochimica Acta **64**(20): 3547-3557.

Concentrations of lignin-phenols were analyzed in high molecular weight dissolved organic matter (0.2 μm > HMW DOM > 1 kDa) isolated from surface waters of the Chesapeake Bay (C. Bay), and surface and bottom waters of the Middle Atlantic Bight (MAB). The abundance of lignin-phenols in HMW DOM was higher in the C. Bay (0.128 +/- 0.06 $\mu\text{g L}^{-1}$) compared to MAB surface waters (0.016 +/- 0.004 $\mu\text{g L}^{-1}$) and MAB bottom waters (0.005 +/- 0.003 $\mu\text{g L}^{-1}$). On an organic carbon-normalized basis, lignin-phenol abundances in the HMW DOM (i.e., Lambda(6)), were significantly higher ($p < 0.05$) in bottom waters compared to sediments at some stations in the MAB. Ratios of syringyl to vanillyl phenols (SN) in HMW DOM, indicative of angiosperm-derived lignin, ranged from 0.165 to 0.422 in C. Bay, 0.100 to 0.314 in MAB surface waters, and 0.076 to 0.357 in MAB bottom waters. Ratios of vanillic acid to vanillin (Ad/Al)(V) in HMW DOM, indicative of lignin decay, ranged from 0.611 to 1.37 in C. Bay, 0.534 to 2.62 in MAB surface waters, and 0.435 to 1.96 in MAB bottom water. Ratios of

SN and (Ad/AI), showed no significant differences between each environment, providing no evidence of any compositionally distinct input of terrestrial organic matter into each environment. When considering depth profiles of suspended particulate matter in the MAB, with C:N ratios, and bulk radiocarbon ages and stable carbon isotopic values in HMW DOM isolated from these areas, two scenarios present themselves regarding the sources and transport of terrestrially derived HMW DOM in the MAB. Scenario #1 assumes that a low amount of refractory terrestrial organic matter and old DOC are uniformly distributed in the oceans, both in surface and bottom waters, and that primary production in surface waters increases DOC with low lignin and younger DOC which degrades easily. In this case, many of the trends in age and biomarker composition likely reflect general patterns of Atlantic Ocean surface and bottom water circulation in the area of the MAB. Scenario 2 assumes terrestrial organic matter in bottom waters of the MAB may have originated from weathered shelf and slope sediments in nearshore areas via a combination of mechanisms (e.g., diffusion, recent resuspension events, and/or desorption of DOM from riverine POM buried deep in these sites) and entered bottom waters offshore in the MAB by diffusion along isopycnal surfaces. These results complement recent work which proposes that transport of DOM across continental shelves may be a significant source of "old" organic matter to the deep ocean. Copyright (C) 2000 Elsevier Science Ltd.

Moncreiff, C. A. and M. J. Sullivan (2001). "Trophic importance of epiphytic algae in subtropical seagrass beds: evidence from multiple stable isotope analyses." Marine Ecology-Progress Series **215**: 93-106.

Multiple stable isotope analyses were employed to examine food web dynamics in a northern Gulf of Mexico seagrass system in which epiphytic algae were the single most important primary productivity component, being responsible for 46 and 60% of total system and benthic primary production, respectively. The seagrass *Halodule wrightii* Ascherson contributed only 13% to total system primary production on an annual basis. Stable isotope ratios of carbon (δ C-13), nitrogen (δ N-15), and sulfur (δ S-34) were measured for producer and consumer samples collected from May 1989 through November 1992. Epiphytes and leaves of *H. wrightii* had distinct δ C-13 values (-17.5 vs -12 parts per thousand, respectively) as well as distinct δ S-34 values parts per thousand (+18 vs +11 parts per thousand, respectively). δ C-13 values for the sand microflora, occasional macroalgae, and phytoplankton were -16, -17, and -22 parts per thousand, respectively; δ N-15 values were lowest for epiphytes and *H. wrightii* (+6 parts per thousand) and highest for phytoplankton (+100 parts per thousand). Virtually all consumers had δ C-13 values that fell within a narrow range of -20 to -15 parts per thousand, which included all δ C-13 values of epiphytes and the sand microflora but none of those for either *H. wrightii* or phytoplankton. Values for δ N-15 for consumers fell within a range of +8 to +16 parts per thousand, spanning herbivorous species with diets of microalgae to carnivorous species feeding at secondary to tertiary levels in the local food webs. Consumer values for δ S-34 ranged from +4 to +20 parts per thousand (mean = 14.2 parts per thousand), and indicate a stronger influence of

seawater-derived sulfate than sediment-associated sulfides. The stable isotope data, in combination with measured high biomass and primary production rates of the epiphytic algae, strongly suggest that these algae are the primary source of organic matter for higher trophic levels in seagrass beds of Mississippi Sound. The contribution of *H. wrightii* to the food web appears to be minimal. The overall picture that has emerged based on the present and previous stable isotope studies is one of the major trophic importance of benthic microalgae (i.e., epiphytic and sediment-associated) in seagrass beds.

Monica, V. S., A. L. J. Alfredo, et al. (2007). "Nutrient fluxes and net metabolism in Lobos coastal lagoon, Mexico." Hidrobiologica **17**(3): 193-202.

Fluxes of nutrients and net metabolism were estimated in coastal lagoon Lobos, a semi-arid subtropical lagoon from Gulf of California, Mexico. Sampling runs were carried out during summer and winter, seawater samples for nutrients were collected in coastal lagoon, offshore and a channel waste-water, physico-chemical parameters were measured in situ. Fluxes of nutrients and net metabolism were estimated using LOICZ biogeochemical model. Flushing time was 5 days in summer and 12 days in winter. Lobos coastal lagoon was a sink of nitrogen in summer (Delta DIN = - 5645 mol day⁽⁻¹⁾) and in winter (Delta DIN 136,575 mol day⁽⁻¹⁾), and it was a source of phosphorus in summer (Delta DIP = + 360 mol day⁽⁻¹⁾) and sink in winter (Delta DIP - 15,809 mol day⁽⁻¹⁾). During summer, Net Ecosystem Metabolism (NEM) of Lobos lagoon was heterotrophic (- 0.38 mmol m⁽⁻²⁾ d⁽⁻¹⁾) and denitrification process was observed (- 0.1 mmol m⁽⁻²⁾ d⁽⁻¹⁾); during winter the NEM was autotrophic (+ 16.49 mmol m⁽⁻²⁾ d⁽⁻¹⁾) and nitrogen fixation process was observed (+ 1.1 mmol m⁽⁻²⁾ d⁽⁻¹⁾). These results suggest the hypothesis that coastal lagoons semi-arids subtropicals from Eastern coast on Gulf of California have seasonal changes, dominant processes of denitrification and net metabolism heterotrophic during summer, while dominant processes of nitrogen fixation and net metabolism autotrophic during winter.

Morse, J. W. and P. M. Eldridge (2007). "A non-steady state diagenetic model for changes in sediment biogeochemistry in response to seasonally hypoxic/anoxic conditions in the "dead zone" of the Louisiana shelf." Marine Chemistry **106**(1-2): 239-255.

Biogeochemical processes occurring near the sediment-water interface can play an important role in the establishment and persistence of hypoxic-to-anoxic conditions in areas of moderate-to-shallow water depth. Results are given in this paper for diagenetic modeling of two sites from the area on the Louisiana shelf west of the Mississippi River Delta known as the "dead zone". This is one of the largest and most studied regions where seasonal coastal hypoxia occurs. The diagenetic model was capable of generating good matches with depth profiles at both sites in the upper 8 cm. Moderate differences between predicted and observed concentrations below this depth are most likely due to the highly non-steady state conditions in this region. The model was, also able to predict extremely low dissolved sulfide concentrations and bacterial sulfate reduction rates that were in good agreement with independent direct observations. A

sensitivity analysis of the model to input parameters showed that the model was much more sensitive to changes in values under hypoxic conditions than norm-oxic or anoxic conditions in the overlying water. Simulations were carried out to first determine how the profiles of sediment porewater parameters and interfacial fluxes would change under differing quasi-steady state conditions where overlying dissolved oxygen concentrations and the rate of bioirrigation were varied. Next a non-steady state simulation was run to investigate how sediment biogeochemistry would change between these conditions during a hypothetical annual cycle. Results demonstrated a clear need to better understand the dynamic relationship among overlying water oxygen concentrations, the behavior of the benthic faunal community responsible for bioirrigation and sediment biogeochemistry. (C) 2006 Elsevier B.V. All rights reserved.

Mulholland, M. R., P. W. Bernhardt, et al. (2006). "Nitrogen fixation and release of fixed nitrogen by *Trichodesmium* spp. in the Gulf of Mexico." *Limnology and Oceanography* **51**(4): 1762-1776.

During a 3-yr study in the Gulf of Mexico, we measured dinitrogen (N₂) fixation and nitrogen (N) release by *Trichodesmium* and compared these rates with water column N demand and the estimated N necessary to support blooms of *Karenia brevis*, a toxic dinoflagellate that severely affects the West Florida shelf. Net and gross N₂ fixation rates were compared in simultaneous incubations using N-15(2) uptake and acetylene reduction, respectively. The difference between net and gross N₂ fixation is assumed to be an approximation of the rate of N release. Results demonstrate that *Trichodesmium* in the Gulf of Mexico are fixing N₂ at high rates and that an average of 52% of this recently fixed N₂ is rapidly released. Calculations suggest that observed densities of *Trichodesmium* can provide enough N to support moderately sized *K. brevis* blooms. Based on other studies where N-15(2) and acetylene reduction were compared directly, it appears that N release from *Trichodesmium* is common but varies in magnitude among environments. In addition, carbon (C) and N-based doubling times for *Dichodesmium* vary among studies and environments. Comparing gross N₂ fixation and C fixation directly, C-based doubling times exceeded N-based doubling times, which suggests an imbalance in elemental turnover or a failure to fully quantify *Trichodesmium* N use.

Mulholland, P. J., G. R. Best, et al. (1997). "Effects of climate change on freshwater ecosystems of the south-eastern United States and the Gulf Coast of Mexico." *Hydrological Processes* **11**(8): 949-970.

The south-eastern United States and Gulf Coast of Mexico is physiographically diverse, although dominated by a broad coastal plain. Much of the region has a humid, warm temperate climate with little seasonality in precipitation but strong seasonality in runoff owing to high rates of summer evapotranspiration. The climate of southern Florida and eastern Mexico is subtropical with a distinct summer wet season and winter dry season. Regional climate models suggest that climate change resulting from a doubling of the pre-industrial levels of

atmospheric CO₂ may increase annual air temperatures by 3-4 degrees C. Changes in precipitation are highly uncertain, but the most probable scenario shows higher levels over all but the northern, interior portions of the region, with increases primarily occurring in summer and occurring as more intense or clustered storms. Despite the increases in precipitation, runoff is likely to decline over much of the region owing to increases in evapotranspiration exceeding increases in precipitation. Only in Florida and the Gulf Coast areas of the US and Mexico are precipitation increases likely to exceed evapotranspiration increases, producing an increase in runoff. However, increases in storm intensity and clustering are likely to result in more extreme hydrographs, with larger peaks in flow but lower baseflows and longer periods of drought. The ecological effects of climate change on freshwaters of the region include: (1) a general increase in rates of primary production, organic matter decomposition and nutrient cycling as a result of higher temperatures and longer growing seasons; (2) reduction in habitat for cool water species, particularly fish and macroinvertebrates in Appalachian streams; (3) reduction in water quality and in suitable habitat in summer owing to lower baseflows and intensification of the temperature-dissolved oxygen squeeze in many rivers and reservoirs; (4) reduction in organic matter storage and loss of organisms during more intense flushing events in some streams and wetlands; (5) shorter periods of inundation of riparian wetlands and greater drying of wetland soils, particularly in northern and inland areas; (6) expansion of subtropical species northwards, including several non-native nuisance species currently confined to southern Florida; (7) expansion of wetlands in Florida and coastal Mexico, but increase in eutrophication of Florida lakes as a result of greater runoff from urban and agricultural areas; and (8) changes in the flushing rate of estuaries that would alter their salinity regimes, stratification and water quality as well as influence productivity in the Gulf of Mexico. Many of the expected climate change effects will exacerbate current anthropogenic stresses on the region's freshwater systems, including increasing demands for water, increasing waste heat loadings and land use changes that alter the quantity and quality of runoff to streams and reservoirs. Research is needed especially in several critical areas: long-term monitoring of key hydrological, chemical and biological properties (particularly water balances in small, forested catchments and temperature-sensitive species); experimental studies of the effects of warming on organisms and ecosystem processes under realistic conditions (e.g. in situ heating experiments); studies of the effects of natural hydrological variation on biological communities; and assessment of the effects of water management activities on organisms and ecosystem processes, including development and testing of management and restoration strategies designed to counteract changes in climate. (C) 1997 by John Wiley & Sons, Ltd.

Murrell, M. C. (2003). "Bacterioplankton dynamics in a subtropical estuary: evidence for substrate limitation." *Aquatic Microbial Ecology* **32**(3): 239-250.

Bacterioplankton abundance and metabolic characteristics were measured along a transect in Pensacola Bay, Florida, USA, to examine the factors that control

microbial water column processes in this subtropical estuary. The microbial measures included H-3-L-leucine incorporation, ectoenzyme activity (aminopeptidase, U-D-glucosidase, P-D-glucosidase) and bacterial abundance. Bacterioplankton abundance ranged from 1.8 to 15.3 x 10⁹ l⁻¹ (average: 6.2 x 10⁶); highest abundances occurred during summer months, particularly in the upper estuary. Bacterial secondary production ranged from 20 to 273 $\mu\text{g C l}^{-1} \text{d}^{-1}$ (average 115), aminopeptidase activities ranged from 34 to 356 nmol l⁻¹ d⁻¹ (average 165), alpha-D-glucosidase ranged from 0.4 to 61 nmol l⁻¹ d⁻¹ (average: 8.3), and beta-D-glucosidase ranged from 1.4 to 53.1 nmol l⁻¹ d⁻¹ (average: 10.5). Bacterioplankton exhibited strong seasonality, suggesting that temperature was an important driver of the observed variability. When normalized for bacterial biomass, metabolic rates exhibited a striking inter-annual pattern with lower rates during summer 2000 than 2001. This pattern was consistent with freshwater flows, which were much lower during 2000 than 2001, consequently lowering nutrient and dissolved organic carbon (DOC) supply to the estuary. These results underscore the importance of riverine flux of materials to support bacterial metabolism and suggest that bacterioplankton were substrate-limited during the low flow period. The empirical relationships between bacterioplankton and phytoplankton variables were similar to those found in literature synthesis studies, with the notable exception that bacterial abundances and production were higher than predicted from chlorophyll a concentration. One explanation for this departure is that these relationships are drawn largely from cool temperate environments and warm subtropical systems are underrepresented in the literature.

Nagao, S., T. Usui, et al. (2005). "Combined use of delta C-14 and delta C-13 values to trace transportation and deposition processes of terrestrial particulate organic matter in coastal marine environments." *Chemical Geology* **218**(1-2): 63-72.

Accelerator mass spectrometry was used to measure radiocarbons of riverine suspended particles and sediments from the estuary, continental shelf and slope off the coast of Tokachi River in Japan. The spatial distribution of Delta(14)C and delta(13)C values of sedimentary organic matter was divided into those of (1) estuary, (2) continental shelf, and (3) continental slope. For shelf sediments, respective maxima can be seen for Delta(14)C value, ON ratio and organic carbon content at a station near the river mouth. The mean grain size of surface sediments also exhibits a similar trend. The delta(13)C values show a minimum near the river mouth. The shelf composition does not appear to be a simple mixture of terrestrial and marine origin. From the above data, it is considered that the spatial distribution of Delta(14)C and delta(13)C values may reflect variations in dispersion and deposition processes together with the size fractionation of riverine suspended particles, the resuspension of sediments, and differences in the contribution of marine organic matter. (c) 2005 Elsevier B.V All rights reserved.

Nelsen, T. A., P. Blackwelder, et al. (1994). "TIME-BASED CORRELATION OF BIOGENIC, LITHOGENIC AND AUTHIGENIC SEDIMENT COMPONENTS WITH

ANTHROPOGENIC INPUTS IN THE GULF-OF-MEXICO - NECOP STUDY AREA." Estuaries **17**(4): 873-885.

Hypotheses related to variability in seasonal hypoxic conditions, coastal nutrient enhancement, and offshore transport of carbon on the Louisiana continental shelf were tested by characterization of biogenic, lithogenic, and authigenic components from two shelf and one Mississippi Canyon sediment cores. The authigenic-phase glauconite occurs above detection limits only in the core from the hypoxic area. A major increase in glauconite concentration was coincident with the onset (similar to 1940) of the increased use of commercial fertilizers in the United States. In the same hypoxic-area core, benthic foraminifera species diversity decreases upcore from approximately the turn of the century to the present in a manner concurrent with glauconite and fertilizer increases. A subset of opportunistic benthic foraminifera species, known to become more prominent in stressed environments (i.e., hypoxic), increased upcore from similar to 52% of the total population at core bottom to similar to 90% at core top. These benthic foraminifera population and diversity changes were not apparent in a "control" core outside the area of documented hypoxia. Seaward of the shelf, in the Mississippi Canyon, coincident increases in sediment accumulation rate, percentages of coarse fraction and of organic carbon at core top indicate increased offshore transport of carbon and other components. Quartz percentages indicate that episodic down-canyon transport has been active to core bottom (prior to the mid 1800s).

Nix, E. R., C. R. Fisher, et al. (1995). "PHYSIOLOGICAL ECOLOGY OF A MUSSEL WITH METHANOTROPHIC ENDOSYMBIONTS AT 3 HYDROCARBON SEEP SITES IN THE GULF-OF-MEXICO." Marine Biology **122**(4): 605-617.

In situ growth rates were determined, using two, 1-yr mark/recapture experiments, conducted between September 1991 and July 1993, for an undescribed mytilid, Seep Mytilid Ia, at three hydrocarbon seep sites in the Gulf of Mexico. The sites are located at depths of 540 to 730 m, approximately 27 degrees 45'N; 91 degrees 30'W, and are separated by distances of 6 to 18 miles. These seep mytilids harbor methanotrophic endosymbionts and use methane as both a carbon and energy source. The mussel habitats were chemically characterized by analysis of water samples taken from precisely located microenvironments over, among and below the mussels, using small-volume, interstitial water samplers and the "Johnson Sea Link" submersible. Substantial differences were found in habitat conditions, growth rates, and population structure for the mussels at the three sites examined. The growth rate of these seep mytilids reflects the methane concentration in their immediate habitat. Mussels at sites with abundant methane had growth rates that were comparable to shallow water mytilids at similar temperatures (5 to 8 degrees C) with increases in shell length up to 17 mm yr⁻¹ documented for smaller mussels (< 40 mm shell length). In conjunction with measurements of growth rates, three condition indices (glycogen content, tissue water content, and the ratio of ash-free dry weight to shell volume) were used to determine the relationship between the condition of the mussels, their growth rates, and their habitat

chemistry. The three condition indices were correlated with growth rate and were often significantly different between mussels in different samples.

Onstad, G. D., D. E. Canfield, et al. (2000). "Sources of particulate organic matter in rivers from the continental USA: Lignin phenol and stable carbon isotope compositions." Geochimica Et Cosmochimica Acta **64**(20): 3539-3546.

The origins and forms of particulate organic matter (POM) suspended in rivers are major considerations in assessing how fluvial materials integrate landscape and climate properties and ultimately record these characteristics in marine sedimentary deposits. We examined the elemental, stable carbon isotope and lignin-phenol compositions of well-characterized samples of suspended POM collected from rivers draining the south central United States. The atomic C/N ratios of 17 fine-grained samples (similar to 11 ± 2 , $n = 17$) are similar to those reported worldwide for texturally similar soil and riverine POM. The corresponding $\delta(13)C$ values vary from -18.5 to -26.4 parts per thousand, in patterns that correspond to the relative abundances of C3 and C4 plants in the drainage basins, and hence to temperature and hydrologic patterns. Lignin-phenol yields from 12 samples indicate input of angiosperm-rich plant materials in distributions that also reflect upstream climate and vegetation. The lignin associated with these plant remains has been substantially degraded, as is typical of soil organic matter. The mass- and surface-area-normalized organic carbon contents of the river-borne POM also correspond to drainage basin properties in patterns characteristic of soils. These results indicate that highly degraded soil organic matter is a major component of fine-grained POM transported by rivers of the central US. The Mississippi River currently discharges "heavy" ($\delta(13)C$ approximate to -20 parts per thousand) lignin-poor POM. The isotopic composition of this organic matter is difficult to distinguish from marine plankton remains in fine-grained sediments of the northern Gulf of Mexico, whose isotopic compositions have been previously interpreted to broadly indicate limited offshore transport of terrigenous organic matter. Copyright (C) 2000 Elsevier Science Ltd.

Orcutt, B. N., A. Boetius, et al. (2004). "Life at the edge of methane ice: microbial cycling of carbon and sulfur in Gulf of Mexico gas hydrates." Chemical Geology **205**(3-4): 239-251.

The processes of methane oxidation and sulfate reduction were examined in subsamples of gas hydrate associated materials collected along the Gulf of Mexico continental slope. Standard radiotracer techniques were used to determine rates of microbial activity in different layers of the hydrate environment, including outer sediment (OS), interface sediment (IS), worm burrow sediment (WB), interior hydrate (IN) and a mixture of hydrate and sediment (MIX). The anaerobic oxidation of methane (AOM) and sulfate reduction (SR) were observed in all hydrate samples examined and the rates of these processes showed similar spatial trends between different hydrate layers. Highest rates of both AOM and SR were observed at interface between the sediment and hydrate. AOM rates were about $3-11 \text{ nmol cm}^{-3} \text{ day}^{-1}$ in worm

burrow and interface sediments as compared to $<1 \text{ nmol cm}^{-3} \text{ day}^{-1}$ in other hydrate material types. Rates of SR ranged from 59 to $490 \text{ nmol cm}^{-3} \text{ day}^{-1}$ in worm burrow and interface sediments while rates in interior hydrate samples were an order of magnitude lower. These rates observed in hydrate materials are lower than rates from nearby methane-rich sediments at ambient temperatures. Nevertheless, our data show that active microbial populations inhabit all layers of the hydrate environment and suggest their activity may impact biogeochemical methane and sulfur cycling in this unique niche. (C) 2004 Elsevier B.V. All rights reserved.

Paerl, H. W., J. Dyble, et al. (2002). "Characterizing man-made and natural modifications of microbial diversity and activity in coastal ecosystems." Antonie Van Leeuwenhoek International Journal of General and Molecular Microbiology **81**(1-4): 487-507.

The impacts of growing coastal pollution and habitat alteration accompanying human encroachment are of great concern at the microbial level, where much of the ocean's primary production and biogeochemical cycling takes place. Coastal ecosystems are also under the influence of natural perturbations such as major storms and flooding. Distinguishing the impacts of natural and human stressors is essential for understanding environmentally-induced change in microbial diversity and function. The objective of this paper is to discuss the applications and merits of recently developed molecular, ecophysiological and analytical indicators and their utility in examining anthropogenic and climatic impacts on the structure and function of coastal microbial communities. The nitrogen-limited Neuse River Estuary and Pamlico Sound, North Carolina are used as examples of ecosystems experiencing both anthropogenic (i.e., accelerating eutrophication) and climatic stress (increasing frequencies of tropical storms and hurricanes). Additional examples are derived from a coastal monitoring site (LEO) on the Atlantic coast of New Jersey and Galveston Bay, on the Gulf of Mexico. In order to assess structure, function, and trophic state of these and other coastal ecosystems, molecular (DNA and RNA-based) characterizations of the microbial taxa involved in carbon, nitrogen and other nutrient transformations can be combined with diagnostic pigment-based indicators of primary producer groups. Application of these methods can reveal process-level microbial community responses to environmental variability over a range of scales. Experimental approaches combined with strategic monitoring utilizing these methods will facilitate: (a) understanding organismal and community responses to environmental change, and (b) synthesizing these responses in the context of ecosystem models that integrate physical, chemical and biotic variability with environmental controls.

Pakulski, J. D. and R. Benner (1994). "ABUNDANCE AND DISTRIBUTION OF CARBOHYDRATES IN THE OCEAN." Limnology and Oceanography **39**(4): 930-940. Carbohydrate concentrations in depth profiles from the Atlantic and Pacific Oceans, the Gulf of Mexico, and the Gerlache Strait (Antarctica) were determined by MBTH analysis without hydrolysis and after hydrolysis with dilute

HCl and concentrated H₂SO₄. Total carbohydrate (TCHO) concentrations in surface waters varied from 7 to 33 μM C and accounted for 21±7% of the dissolved organic carbon (DOC) measured by high-temperature combustion. Polysaccharides (PCHO) were the dominant form of carbohydrate in waters above oxygen minima whereas monosaccharides were dominant in the deep ocean. PCHO comprised 71±18% of TCHO and 16±9% of the DOC above oxygen minima at all stations. Hydrolysis-resistant PCHO comprised 67±30% of the total PCHO. Monosaccharide (MCHO) concentrations averaged 4.3±1.9 μM C and varied little with depth at all stations. The large (5-fold) decrease in PCHO concentrations between surface waters and oxygen minima suggested that polysaccharides are an active component of the carbon cycle in the upper ocean.

Pakulski, J. D., R. Benner, et al. (2000). "Microbial metabolism and nutrient cycling in the Mississippi and Atchafalaya River plumes." Estuarine Coastal and Shelf Science **50**(2): 173-184.

Spatial distributions of chlorophyll, bacterial abundances and production, community respiration, and dissolved C, N, P and Si were measured in the Mississippi River (MRP) and Atchafalaya River (ARP) plumes during July 1993. Dark bottle incubations were used to estimate net flux rates of inorganic nutrients, community respiration, and changes in chlorophyll concentrations in unfiltered water samples. Concentrations of total dissolved N (TDN) and soluble reactive P (SRP) in the Mississippi River were 55 μM and 3 μM higher, respectively, compared with those in the Atchafalaya River. Concentrations of dissolved organic carbon (DOC) and nitrogen (DON) in the Atchafalaya River, however, were 35 and 11 μM higher, respectively than in the Mississippi River. Elevated chlorophyll concentrations, bacterial abundances and production, and community respiration rates were observed at intermediate (5-25) salinities of both plumes. Property-salinity plots indicated net sinks of dissolved N, P and Si at intermediate salinities consistent with photosynthetic utilization of these substances within the plumes. The distribution of dissolved P, N and chlorophyll suggested phytoplankton-mediated transformation of riverine-NO₃⁻ to DON at intermediate salinities of the MRP, and a similar transformation of riverine SRP to dissolved organic P (DOP) at intermediate salinities of the ARP. Net regeneration of dissolved Si and NH₄⁺ was observed in regions of elevated chlorophyll concentrations and net removal rates in both plumes. Nitrification rates in the MRP were c. 10-fold higher than in the ARP. Estimates of C fixation by nitrifying bacteria equalled or exceeded heterotrophic bacterial C production in the low salinity region of the MRP, but were negligible compared to heterotrophic bacterial production in the ARP. Dissolved inorganic N:P, Si:P and DOC:DON:DOP ratios suggested the potential for P limitation in both plume systems during the period investigated. (C) 2000 Academic Press.

Pancost, R. D. and C. S. Boot (2004). "The palaeoclimatic utility of terrestrial biomarkers in marine sediments." Marine Chemistry **92**(1-4): 239-261.

Organic compounds of known biological origin (biomarkers) and preserved in

marine sediments have commonly been used to develop proxy records for past climate. While biomarkers for marine organisms are the logical target of many investigations, higher plant and other terrestrial biomarkers are also common in marine sediments and can be used to develop records of past continental vegetation, from which climatic change can be inferred. In fact, the high sampling resolution and extensive temporal record (>100 ma) of marine sediments, combined with the fact that compounds in marine sediments are delivered from a potentially vast geographical area, means that marine sediments can be more appropriate for such investigations than comparable terrestrial sedimentary sequences (lacustrine sediments, peats). Critical challenges to this approach include elucidation of the controls on delivery of organic material to marine sediments, ecological and physiological variability in biomarker distributions and isotopic compositions and the impact of diagenetic alteration on biomarker distributions. Here, we review potential terrestrial plant and microbial biomarkers, the controls on their carbon isotopic compositions and their modes of delivery to marine sediments, devoting specific attention to their utility in continental vegetation reconstruction. (C) 2004 Elsevier B.V. All rights reserved.

Pancost, R. D., C. L. L. Zhang, et al. (2005). "Lipid biomarkers preserved in hydrate-associated authigenic carbonate rocks of the Gulf of Mexico." Palaeogeography Palaeoclimatology Palaeoecology **227**(1-3): 48-66.

Anaerobic oxidation of methane (AOM) is common in ocean-margin sediments, where it is mediated by consortia of Archaea and Bacteria and can result in the formation of authigenic carbonate, including extensive carbonate crusts. Previous work indicates that AOM is associated with Gulf of Mexico hydrocarbon seeps and is mediated by similar organisms as identified in other settings; however, biological investigations have not been done on the associated C-13-depleted carbonates. Here, we show that C-13-depleted archaeal and bacterial biomarkers are abundant in Gulf of Mexico authigenic carbonate rocks, revealing that AOM-mediating organisms are closely associated with carbonate authigenesis. Moreover, the rocks share general characteristics of the background (soft) sedimentary archaeal and bacterial community inferred from biomarker analysis, suggesting that the organisms associated with carbonate authigenesis are the same as those that live elsewhere in the hydrocarbon seep environment. This provides further evidence that AOM by Archaea and sulfate-reducing bacteria can result in the sequestration of significant quantities of methane-derived carbon in carbonate rocks. (c) 2005 Elsevier B.V. All rights reserved.

Park, Y., D. Y. Kim, et al. (2006). "Sequestering carbon dioxide into complex structures of naturally occurring gas hydrates." Proceedings of the National Academy of Sciences of the United States of America **103**(34): 12690-12694.

Large amounts of CH₄ in the form of solid hydrates are stored on continental margins and in permafrost regions. If these CH₄ hydrates could be converted into CO₂ hydrates, they would serve double duty as CH₄ sources and CO₂ storage sites. We explore here the swapping phenomenon occurring in structure I

(sl) and structure II (sII) CH₄ hydrate deposits through spectroscopic analyses and its potential application to CO₂ sequestration at the preliminary phase. The present 85% CH₄ recovery rate in sI CH₄ hydrate achieved by the direct use of binary N₂ + CO₂ guests is surprising when compared with the rate of 64% for a pure CO₂ guest attained in the previous approach. The direct use of a mixture of N₂ + CO₂ eliminates the requirement of a CO₂ separation/purification process. In addition, the simultaneously occurring dual mechanism of CO₂ sequestration and CH₄ recovery is expected to provide the physicochemical background required for developing a promising large-scale approach with economic feasibility. In the case of sII CH₄ hydrates, we observe a spontaneous structure transition of sII to sI during the replacement and a cage-specific distribution of guest molecules. A significant change of the lattice dimension caused by structure transformation induces a relative number of small cage sites to reduce, resulting in the considerable increase of CH₄ recovery rate. The mutually interactive pattern of targeted guest-cage conjugates possesses important implications for the diverse hydrate-based inclusion phenomena as illustrated in the swapping process between CO₂ stream and complex CH₄ hydrate structure.

Parker, P. L., D. Shultz, et al. (1972). "STABLE CARBON ISOTOPE RATIO VARIATIONS IN ORGANIC CARBON FROM GULF OF MEXICO SEDIMENTS." Contributions in Marine Science **16**(MAR): 139-&.

Passow, U., J. Dunne, et al. (2006). "Organic carbon to Th-234 ratios of marine organic matter." Marine Chemistry **100**(3-4): 323-336.

Uncertainties in the determinations of particulate organic carbon flux from measurements of the disequilibrium between Th-234 and its mother isotope uranium depend largely on the determination of the organic carbon to (234)thorium (OC : Th-234) ratio. The variability of the OC : Th-234 ratio in different size fractions of suspended matter, ranging from the truly dissolved (< 3 or 10 kDa) fraction to several millimeter sized marine snow, as well as from sediment trap material was assessed during an eight-day cruise off the coast of California in Spring 1997. The affinity of polysaccharide particles called TEP (transparent exopolymer particles) and inorganic clays to Th-234 was investigated through correlations. The observed decrease in the OC : Th-234 ratio with size, within the truly dissolved to small particle size range, is consistent with concepts of irreversible colloidal aggregation of non-porous nano-aggregates. No consistent trend in the OC : Th-234 ratio was observed for particles between 1 or 10 to 6000 μm . Origin and fate of marine particles belonging to this size range are diverse and interactions with Th-234 too complex to expect a consistent relationship between OC : Th-234 ratio and size, if all categories of particles are included. The relationship between OC and Th-234 was significant when data from the truly dissolved fraction were excluded. However, variability was very large, implying that OC flux calculations using different collection methods (e.g. sediment trap, Niskin bottles or pumps) would differ significantly. Therefore a large uncertainty in OC flux calculations based on the Th-234 method exist due to individual decisions as to which types or size

classes of particles best represent sinking material in a specific area. Preferential binding of Th-234 to specific substance classes could explain the high variability in the relationship between OC and Th-234. At 15 m, in the absence of lithogenic material, the OC : Th-234 ratio was a function of the fraction of TEP or TEP-precursors in OC, confirming that acidic polysaccharides have a high affinity for Th-234 and that TEP carry a ligand for Th-234. Preferential binding to TEP might change distribution patterns of Th-234 considerably, as TEP may sink when included in large aggregates, or remain suspended or even ascend when existing as individual particles or microaggregates. In the presence of lithogenic matter, at depths below 30 m, the ratio between Th-234 and OC was linearly related to the ratio between aluminosilicates and C. The affinity of inorganic substances to Th-234 is known to be relatively low, suggesting that a coating of acidic polysaccharides was responsible for the apparently high affinity between Th-234 and lithogenic material. Overall, OC : Th-234 ratios of all material collected during this investigation can best be explained by differential binding of Th-234 to both TEP and TEP-precursors, as well as to lithogenic minerals, which were very abundant in an intermediate nepheloid layer between 50 and 90 m. (c) 2005 Elsevier B.V. All rights reserved.

Pattanayak, S. K., B. A. McCarl, et al. (2005). "Water quality co-effects of greenhouse gas mitigation in US agriculture." Climatic Change **71**(3): 341-372.

This study develops first-order estimates of water quality co-effects of terrestrial greenhouse gas (GHG) emission offset strategies in U.S. agriculture by linking a national level agricultural sector model (ASMGHG) to a national level water quality model (NWPCAM). The simulated policy scenario considers GHG mitigation incentive payments of \$25 and \$50 per tonne, carbon equivalent to landowners for reducing emissions or enhancing the sequestration of GHG through agricultural and land-use practices. ASMGHG projects that these GHG price incentives could induce widespread conversion of agricultural to forested lands, along with alteration of tillage practices, crop mix on land remaining in agriculture, and livestock management. This study focuses on changes in cropland use and management. The results indicate that through agricultural cropland about 60 to 70 million tonnes of carbon equivalent (MMTCE) emissions can be mitigated annually in the U.S. These responses also lead to a 2% increase in aggregate national water quality, with substantial variation across regions. Such GHG mitigation activities are found to reduce annual nitrogen loadings into the Gulf of Mexico by up to one half of the reduction goals established by the national Watershed Nutrient Task Force for addressing the hypoxia problem.

Patzek, T. W. (2004). "Thermodynamics of the corn-ethanol biofuel cycle." Critical Reviews in Plant Sciences **23**(6): 519-567.

This article defines sustainability and sustainable cyclic processes, and quantifies the degree of non-renewability of a major biofuel: ethanol produced from industrially grown corn. It demonstrates that more fossil energy is used to produce ethanol from corn than the ethanol's calorific value. Analysis of the

carbon cycle shows that all leftovers from ethanol production must be returned back to the fields to limit the irreversible mining of soil humus. Thus, production of ethanol from whole plants is unsustainable. In 2004, ethanol production from corn will generate 8 million tons of incremental CO₂, over and above the amount Of CO₂ generated by burning gasoline with 115% of the calorific value of this ethanol. It next calculates the cumulative exergy (available free energy) consumed in corn farming and ethanol production, and estimates the minimum amount of work necessary to restore the key non-renewable resources consumed by the industrial corn-ethanol cycle. This amount of work is compared with the maximum useful work obtained from the industrial corn-ethanol cycle. It appears that if the corn-ethanol exergy is used to power a car engine, the minimum restoration work is about 6 times the maximum useful work from the cycle. This ratio drops down to 2 if an ideal fuel cell is used to process the ethanol. The article estimates the U.S. taxpayer subsidies of the industrial corn-ethanol cycle at \$3.8 billion in 2004. The parallel subsidies by the environment are estimated at \$1.8 billion in 2004. The latter estimate will increase manifold when the restoration costs of aquifers, streams, and rivers, and the Gulf of Mexico are also included. Finally, the article estimates that (per year and unit area) the inefficient solar cells produce similar to 100 times more electricity than corn ethanol. There is a need for more reliance on sunlight, the only source of renewable energy on the earth.

Pease, T. K., E. S. Vanvleet, et al. (1992). "DIPHYTANYL GLYCEROL ETHER DISTRIBUTIONS IN SEDIMENTS OF THE ORCA BASIN." Geochimica Et Cosmochimica Acta **56**(9): 3469-3479.

Archaeobacterially produced diphytanyl glycerol ether (DPGE) was examined in core sediments from the Orca Basin, an anoxic hypersaline basin in the northwestern Gulf of Mexico, to observe its spatial variability and potential origin. A differential extraction protocol was employed to quantify the isopranyl glycerol ethers associated with unbound, intermediate-bound, and kerogen-bound lipid fractions. Archaeobacterial lipids were evident at all depths for the unbound and intermediate-bound fractions. Concentrations of DPGE ranged from 0.51 to 2.91 mug/g dry sediment at the surface and showed secondary maxima deeper in basin sediments. Intermediate-bound DPGE concentrations exhibited an inverse relationship to unbound DPGE concentrations. Kerogen-bound DPGE concentrations were normally below detection limits. Earlier studies describing the general homogeneity of lipid components within the overlying brine and at the brine/seawater interface suggest that the large-scale sedimentary DPGE variations observed in this study result from spatial and temporal variations in in situ production by methanogenic or extremely halophilic archaeobacteria.

Perez, B. C., J. W. Day, et al. (2000). "Influence of Atchafalaya River discharge and Winter frontal passage on suspended sediment concentration and flux in Fourleague Bay, Louisiana." Estuarine Coastal and Shelf Science **50**(2): 271-290.

Suspended sediment concentrations and fluxes between Fourleague Bay, Louisiana and the northern Gulf of Mexico were sampled every 3 h for 3 months

to examine the importance of atmospheric cold fronts and riverine forcing on the functioning of this estuarine system. A cold front index was developed and used to identify major winter frontal passages likely to have the largest effects on material concentrations and transport. Suspended sediment concentrations ranged from 11 to 1527 mg l⁻¹; the highest values occurred during winter frontal passages and the lowest during calm periods. High concentrations are generated by a continuous source of sediment from the Atchafalaya River and resuspension of benthic sediment via high intensity winds associated with cold fronts along with sufficient duration to keep the sediment in suspension. Spring peak discharge of the Atchafalaya River increased water levels and sediment concentrations in the bay leading to strong seasonal net exports of water (1.02×10^9 m³) and sediment (1.72×10^8 kg) into the Gulf of Mexico through Oyster Bayou over the 89-day study. Net fluxes associated with tidal forcing were nearly balanced with a small net export due to freshwater input. The combination of high volumes of water originating from the northern bay and the restricted outlet to the Gulf often cause increased water levels and inundation of the surrounding marshes and potential advection of sediments onto the marsh surface. The results suggest that marsh drainage often increases the particulate organic carbon export as a result of marsh flushing. (C) 2000 Academic Press.

Phoel, W. C., G. T. Rowe, et al. (1993). "SEDIMENT CHARACTERISTIC OF THE CONTINENTAL-SHELF IN THE NORTHERN GULF-OF-MEXICO." Revista De Biologia Tropical **41**: 49-52.

Pomeroy, L. R., J. E. Sheldon, et al. (2000). "Seasonal changes in microbial processes in estuarine and continental shelf waters of the south-eastern USA." Estuarine Coastal and Shelf Science **51**(4): 415-428.

Respiratory rates of microbial plankton in five estuaries of Georgia, U.S.A. are similar at any given time of year, both within and among the estuaries, but change from 0.16 ± 0.02 $\mu\text{M h}^{-1}$ (mean \pm SE) in winter to 0.95 ± 0.08 $\mu\text{M h}^{-1}$ in summer, following the Arrhenius law. In short-term enrichment experiments, heterotrophs respond to added labile carbon, thus indicating a dual temperature-substrate limitation. The relatively much greater microbial metabolic rates in the marsh sediments than in estuarine water, the dominance of estuarine primary production in south-eastern U.S.A. by higher plants, and limited phytoplankton production in turbid water may explain the carbon limitation.

Respiratory rates of south-eastern U.S.A. continental shelf microbial plankton are 1.1 ± 0.14 $\mu\text{M h}^{-1}$ near shore in winter and 0.95 ± 0.08 $\mu\text{M O}_2 \text{ h}^{-1}$ in summer. In mid-shelf they are 0.7 ± 0.11 in winter and 1.3 ± 0.28 in summer, and at the edge of the Gulf Stream they are 0.3 ± 0.1 in winter and 1.0 ± 0.3 in summer. Thus, in contrast to the estuaries, microbial respiration in shelf waters is as high throughout the year as estuarine respiration in summer, showing no significant seasonal change, but: respiration in the Gulf Stream changes seasonally. Although primary production on the south-eastern shelf is relatively high, especially near shore and in intrusions of North Atlantic Central Water, no correlation was found between respiratory rates of microbial plankton and

concentrations of chlorophyll a. Concentrations of dissolved free amino acids in continental shelf waters are 39-87 nM with no evident seasonal cycle. Compared to other estuarine-shelf systems, the south-eastern system is known not to be highly productive of higher trophic levels, i.e. fishes and shellfish. We postulate that this is a result of the trophic structure on the south-eastern U.S. continental shelf system which in turn is a consequence of the distribution of macronutrients, principally nitrogen. Most new nitrogen is from the North Atlantic Central Water rather than from terrestrial sources and, therefore, it is less well distributed over the central shelf. (C) 2000 Academic Press.

Pomeroy, L. R., J. E. Sheldon, et al. (1995). "LIMITS TO GROWTH AND RESPIRATION OF BACTERIOPLANKTON IN THE GULF-OF-MEXICO." Marine Ecology-Progress Series **117**(1-3): 259-268.

We compared microbial community respiration and related parameters in the Gulf of Mexico in January and June 1993. Microbial community respiratory rates in the upper mixed layer varied from $<0.03 \mu\text{M O}_2 \text{ h}^{-1}$ in the central Gulf in January to $1.4 \mu\text{M O}_2 \text{ h}^{-1}$ in the Mississippi River plume in June. Although higher respiratory rates were found in June than in January, no significant differences were found in bacterial numbers or mean cell volume. Dissolved free amino acid concentrations were an order of magnitude higher in June, but there was little difference in concentrations of phosphate or monosaccharides between January and June. Enrichment experiments in June showed phosphate to be the primary limiting factor for bacterial production and microbial community respiration and organic carbon substrates to be a secondary limiting factor. Respiratory rate and bacterial secondary production increased when phosphate was added to water samples. Ammonium, iron and other trace metals, vitamins and chelators had no effect. Glucose was utilized only when supplemented with phosphate. Turnover time of bacterial biomass in June, based on counts, sizes, and production data, was 7 to 30 h, with the shortest times at oligotrophic stations. The observed rates of bacterial respiration and production imply the utilization of multiple sources of organic and recycled inorganic nutrients in a complex and inefficient food web.

Putland, J. N. and R. L. Iverson (2007). "Phytoplankton biomass in a subtropical estuary: Distribution, size composition, and carbon : chlorophyll ratios." Estuaries and Coasts **30**(5): 878-885.

The seasonal pattern of phytoplankton biomass (chlorophyll and particulate organic carbon) and the salinity-related pattern of phytoplankton biomass and size composition were determined in Apalachicola Bay, Florida, throughout 2004. Phytoplankton biomass was highest during summer and lowest during winter. During summer, phytoplankton biomass was highest in waters with salinity between about 5 and 23. In waters between 5 and 23, phytoplankton biomass was primarily (> 50%) composed of $< 5 \mu\text{m}$ cells. The results from this study support the idea that a microbial food web characterizes mass and energy flow through the planktonic food web in Apalachicola Bay and other estuaries. During winter, the carbon:chlorophyll a ratio averaged 56 ± 60 (standard deviation).

During summer, the ratio ranged from 23 to 345, with highest values occurring in waters with salinity between about 8 and 22. The carbon:chlorophyll a ratio was positively related to the percent of chlorophyll $\lt; \mu 5\text{ m}$ in size during summer.

Qian, Y., M. C. Kennicutt, et al. (1996). "Suspended particulate organic matter (SPOM) in Gulf of Mexico estuaries: Compound-specific isotope analysis and plant pigment compositions." Organic Geochemistry **24**(8-9): 875-888.

Pigment and stable isotopic compositions of suspended particulate organic matter (SPOM) were determined in several estuaries along the Texas coast of the Gulf of Mexico. Analysis of the composition of accessory pigments suggested that the phytoplankton taxa varied among these bays. The $\delta(13)\text{C}$ values of SPOM, lipids, and chlorophylls in these bays varied from - 18 to - 27, - 20 to - 31, and - 18 to - 31 parts per thousand, respectively. The $\delta(13)\text{C}$ Values of SPOM, lipids, and chlorophylls, and the pigment composition together suggest that the C-13-depleted organic matter in Corpus Christi Bay in June 1992 resulted from the fixation of C-13-depleted CO_2 derived from riverine water or in Situ remineralization of organic matter. The lipids and chlorophyll a isolated from the nearly freshwater system of Aransas Bay in 1992 were C-13-enriched and most likely derived from local phytoplankton production. The $\delta(13)\text{C}$ values of SPOM, lipids and chlorophylls in the bays where salinities were closest to that of seawater were in the range expected for marine phytoplankton, i.e., - 18 to - 24 parts per thousand. The $\delta(13)\text{N}$ values for SPOM, lipids, and chlorophyll a ranged from + 4 to + 14 parts per thousand with most between + 6 to + 10 parts per thousand. These values are similar to the SPOM of marine systems and indicate a common source of nitrogen throughout the estuaries. Copyright (C) 1996 Elsevier Science Ltd

Rabalais, N. N., N. Atilla, et al. (2004). "Ecosystem history of Mississippi River-influenced continental shelf revealed through preserved phytoplankton pigments." Marine Pollution Bulletin **49**(7-8): 537-547.

Pigments determined by high performance liquid chromatography (HPLC) provide useful information concerning water column and epibenthic plant and microbial communities in both extant communities and accumulated sediments in lakes, estuaries and the ocean. Chlorophyll and its degradation products provide an estimate of overall biomass, and carotenoid pigments provide taxonomic biomarkers of phytoplankton. We examined the pigments preserved in sediment cores from the Louisiana continental shelf adjacent to the outflow of the Mississippi River system to document changes in phytoplankton community composition, phytoplankton abundance, and conditions of hypoxia over time. Carbon accumulated in sediments from water depths of 20-60 m is primarily derived from marine phytoplankton and represents the history of phytoplankton communities in the overlying water. There is a general increase in chlorophyll a, pheopigments, zeaxanthin, fucoxanthin and most carotenoids over time, with the change gradual from 1955 to 1970, followed by a fairly steady increase to 1997. The highest chloropigment concentrations are in cores from areas more likely to be exposed to seasonal hypoxia. These indicate an increase in eutrophication in

the form of greater diatom and cyanobacterial production, or a worsening of hypoxia, or both. This trend expanded westward along the Louisiana shelf in the 1990s. (C) 2004 Elsevier Ltd. All rights reserved.

Rabalais, N. N., R. E. Turner, et al. (2007). "Hypoxia in the northern Gulf of Mexico: Does the science support the plan to reduce, mitigate, and control hypoxia?" Estuaries and Coasts **30**(5): 753-772.

We update and reevaluate the scientific information on the distribution, history, and causes of continental shelf hypoxia that supports the 2001 Action Plan for Reducing, Mitigating, and Controlling Hypoxia in the Northern Gulf of Mexico (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force 2001), incorporating data, publications, and research results produced since the 1999 integrated assessment. The metric of mid-summer hypoxic area on the Louisiana-Texas shelf is an adequate and suitable measure for continued efforts to reduce nutrients loads from the Mississippi River and hypoxia in the northern Gulf of Mexico as outlined in the Action Plan. More frequent measurements of simple metrics (e.g., area and volume) from late spring through late summer would ensure that the metric is representative of the system in any given year and useful in a public discourse of conditions and causes. The long-term data on hypoxia, sources of nutrients, associated biological parameters, and paleoindicators continue to verify and strengthen the relationship between the nitrate-nitrogen load of the Mississippi River, the extent of hypoxia, and changes in the coastal ecosystem (eutrophication and worsening hypoxia). Multiple lines of evidence, some of them representing independent data sources, are consistent with the big picture pattern of increased eutrophication as a result of long-term nutrient increases that result in excess carbon production and accumulation and, ultimately, bottom water hypoxia. The additional findings arising since 1999 strengthen the science supporting the Action Plan that focuses on reducing nutrient loads, primarily nitrogen, through multiple actions to reduce the size of the hypoxic zone in the northern Gulf of Mexico.

Rabalais, N. N., R. E. Turner, et al. (2007). "Sediments tell the history of eutrophication and hypoxia in the Northern Gulf of Mexico." Ecological Applications **17**(5): S129-S143. We examined a suite of paleoindicators in Pb-210-dated sediment cores to determine the historical course of primary production, eutrophication, and oxygen stress in the coastal ocean adjacent to the plumes of the Mississippi and Atchafalaya rivers. The assumption that hypoxia is a natural feature of the coastal ecosystem in the northern Gulf of Mexico influenced by the discharge of the Mississippi River system is not supported by paleoindicators in accumulated sediments. There is a propensity for the ecosystem to develop hypoxia because of the high discharge of the Mississippi River and physical dynamics on the continental shelf that support stratification. However, paleoindicators of eutrophication and oxygen conditions record recent anthropogenic influences. The evidence for increased carbon production and accumulation comes from diatoms and their remnants, marine-origin carbon in the sediments, and phytoplankton pigments. Surrogates for oxygen condition, including mineral,

isotopic, microfossil, and phytoplankton pigment indicators, indicate worsening oxygen stress. The changes are more apparent in areas of present chronic hypoxia and are coincident with the increasing nitrogen loads from the Mississippi River system beginning in the 1950s. Longer-term shifts in offshore ecology parallel landscape changes within the watershed in the last two centuries. The temporal shifts in this coastal ecosystem parallel the time sequence of similarly eutrophied coastal waters globally and coincide nicely with sediment analyses from other locations.

Rabalais, N. N., R. E. Turner, et al. (2001). "Hypoxia in the Gulf of Mexico." Journal of Environmental Quality **30**(2): 320-329.

Seasonally severe and persistent hypoxia, or low dissolved oxygen concentration, occurs on the inner- to mid-Louisiana continental shelf to the west of the Mississippi River and Atchafalaya River deltas. The estimated areal extent of bottom dissolved oxygen concentration less than 2 mg L⁻¹ during mid-summer surveys of 1993-2000 reached as high as 16 000 to 20 000 km². The distribution for a similar mapping grid for 1985 to 1992 averaged 8000 to 9000 km². Hypoxia occurs below the pycnocline from as early as late February through early October, but is most widespread, persistent, and severe in June, July, and August. Spatial and temporal variability in the distribution of hypoxia exists and is, at least partially, related to the amplitude and phasing of the Mississippi and Atchafalaya discharges and their nutrient flux. Mississippi River nutrient concentrations and loadings to the adjacent continental shelf have changed dramatically this century, with an acceleration of these changes since the 1950s to 1960s. An analysis of diatoms, foraminiferans, and carbon accumulation in the sedimentary record provides evidence of increased eutrophication and hypoxia in the Mississippi River delta bight coincident with changes in nitrogen loading.

Raymond, P. A. and J. E. Bauer (2001). "Use of C-14 and C-13 natural abundances for evaluating riverine, estuarine, and coastal DOC and POC sources and cycling: a review and synthesis." Organic Geochemistry **32**(4): 469-485.

Though not typically regarded as "biomarkers" in the traditional sense of the word, the radioactive and stable isotopes of carbon (C-14 and C-13, respectively) can serve as powerful tools for identifying sources and estimating turnover times of organic matter in aquatic systems. paired C-14 and C-13 measurements of carbon pools can provide an additional degree of specificity for studies of organic matter cycling as a result of: (1) the lower susceptibility of natural isotopes to diagenetic effects that can alter organic biomolecules; (2) the "dual" isotopic nature of the approach; (3) the unique input functions for each isotope; and (4) the greater dynamic range in Delta C-14 (-1000 to similar to +200 parts per thousand) compared to delta C-13 (similar to -32 to -12 parts per thousand). Relatively few geochemical studies in rivers, estuaries and the coastal ocean Waters have employed C-14 and C-13 analyses of organic matter. In this paper we summarize the available data on C-14 and C-13 measurements in dissolved and particulate organic carbon (DOC and POC, respectively) in these systems. A

brief review is presented of current methods for the separation and oxidation of DOC and POC from water samples, for subsequent Delta C-14 and delta C-13 analyses. We also compile the existing datasets on paired C-14 and C-13 measurements across the riverine to coastal marine continuum in order to elucidate sources, ages, and transformations of organic matter within each system, and during transport from rivers to the coastal ocean. The natural range in the Delta C-14 values of both DOC and POC across similar system types was 500 and 1000 parts per thousand, respectively. In general, riverine DOC was enriched in C-14 relative to POC in rivers and estuaries, but the opposite generally held for coastal marine waters. This is indicative of the different sources and transport mechanisms for DOC and POC within and across these three general types of systems. During river and estuarine transport, DOC generally becomes enriched in C-13 and depleted in C-14 due to simultaneous additions from autochthonous production and removals from heterotrophic bacteria and abiotic processes. Bacterial utilization experiments indicate that bacteria preferentially utilize a C-14 enriched (i.e. young) DOC fraction and, therefore, DOC utilization is a partial explanation for the C-14-depleted riverine and estuarine DOC. It is concluded that through the use of paired C-14 and C-13 measurements in DOC and POC, a more robust interpretation of sources, sinks, and residence times of organic matter may be attained than by using either isotope separately. (C) 2001 Elsevier science Ltd. All rights reserved.

Raymond, P. A., N. H. Oh, et al. (2008). "Anthropogenically enhanced fluxes of water and carbon from the Mississippi River." Nature **451**(7177): 449-452.

The water and dissolved inorganic carbon exported by rivers are important net fluxes that connect terrestrial and oceanic water and carbon reservoirs(1). For most rivers, the majority of dissolved inorganic carbon is in the form of bicarbonate. The riverine bicarbonate flux originates mainly from the dissolution of rock minerals by soil water carbon dioxide, a process called chemical weathering, which controls the buffering capacity and mineral content of receiving streams and rivers(2). Here we introduce an unprecedented high-temporal- resolution, 100- year data set from the Mississippi River and couple it with sub- watershed and precipitation data to reveal that the large increase in bicarbonate flux that has occurred over the past 50 years (ref. 3) is clearly anthropogenically driven. We show that the increase in bicarbonate and water fluxes is caused mainly by an increase in discharge from agricultural watersheds that has not been balanced by a rise in precipitation, which is also relevant to nutrient and pesticide fluxes to the Gulf of Mexico. These findings demonstrate that alterations in chemical weathering are relevant to improving contemporary biogeochemical budgets. Furthermore, land use change and management were arguably more important than changes in climate and plant CO₂ fertilization to increases in riverine water and carbon export from this large region over the past 50 years.

Reeburgh, W. S. (2007). "Oceanic methane biogeochemistry." Chemical Reviews **107**(2): 486-513.

Requejo, A. G., J. S. Brown, et al. (1991). "LIGNIN GEOCHEMISTRY OF NORTH-AMERICAN COASTAL AND CONTINENTAL-SHELF SEDIMENTS." Organic Geochemistry **17**(5): 649-662.

The concentrations and composition of lignin in coastal and shelf sediments at five locations along the North American continent-Georges Bank/North Atlantic shelf, northwestern Gulf of Mexico, Southern California, Norton Sound and nearshore Beaufort Sea-have been characterized using alkaline CuO oxidation. Lignin concentrations are generally highest at close proximity to the mouth of major rivers, indicating that deposition of river-borne vascular plant debris is the principal source of lignin to the offshore sediments. Arctic sediments contain the highest concentrations, presumably as a result of an abundant supply of terrestrial organic material and the prevalence of frigid temperatures and surface ice cover during much of the year. Concentrations are lowest in the Georges Bank/North Atlantic sediments, where a dynamic physical environment persists over much of the year and the supply of terrestrial organic matter to the offshore in the form of major rivers is lacking. Stable carbon isotopic compositions show that sediments containing the highest lignin concentrations also contain isotopically-lighter organic matter, consistent with a terrestrial source input. Vanillyl, syringyl and cinnamyl phenol distributions in these offshore sediments are consistent with primary contributions from gymnosperm (predominant) and angiosperm woods and secondary contributions from nonwoody tissues. These estimates may be subject to some uncertainty due to diagenetic alteration of individual lignin phenols. In contrast, p-hydroxyl phenol yields are not strongly correlated with those of the other lignin-derived phenols, suggesting generation from both lignin and non-lignin sources. Elevated acid/aldehyde ratios relative to undegraded plant tissues suggest that the lignin transported to these offshore sediments has undergone some biodegradative oxidation.

Rinker, K. R. and R. T. Powell (2006). "Dissolved organic phosphorus in the Mississippi River plume during spring and fall 2002." Marine Chemistry **102**(1-2): 170-179.

Dissolved organic phosphorus (DOP) may play an important role in controlling primary productivity in coastal systems. In an attempt to understand the controls on seasonal and spatial variability in the Mississippi River plume, DOP samples were collected during spring and fall 2002. DOP concentrations were determined using an autoanalyzer with in-line thermal/UV oxidation. For both seasons, DOP concentrations were highest in the river and decreased with distance from the river. Salinity, chlorophyll a, dissolved organic carbon and nitrogen are parameters which have been shown to correlate with DOP in other systems. Within the Mississippi River plume, no correlation was found between DOP and any of these parameters, and less than 5% of the total dissolved phosphorus was high molecular weight, as separated by tangential flow ultrafiltration. Our results suggest that DOP may cycle quickly in the plume and be a source of inorganic phosphorus in the late summer, leading to seasonal changes in the inorganic N/P ratio and potentially a shift in the planktonic community. (c) 2006 Elsevier B.V. All rights reserved.

Roberts, H. H. and P. Aharon (1994). "HYDROCARBON-DERIVED CARBONATE BUILDUPS OF THE NORTHERN GULF-OF-MEXICO CONTINENTAL-SLOPE - A REVIEW OF SUBMERSIBLE INVESTIGATIONS." Geo-Marine Letters **14**(2-3): 135-148.

Hydrocarbon-derived and microbially mediated authigenic carbonates occur over the entire depth range of the northern Gulf of Mexico slope. These carbonates consist of nodules and incipient nodules in surface sediments, hardgrounds and isolated slabs, and moundlike buildups of up to 10-20 m relief above the surrounding seafloor. The authigenic carbonates are characterized by $\delta^{13}\text{C}$ negative values in the range -18 parts per thousand to -55 parts per thousand (PDB) suggesting mixing of seawater carbon with C-13-depleted carbon sources ranging from crude oil to biogenic methane. Near the shelf edge, carbonates are "diluted" with biogenic material produced by reefs-bioherms developed at low sea level stands. Fossil-poor carbonates over salt diapirs of the upper and middle slope formed in the shallow subsurface and have been exhumed by the combined processes of uplift and physical erosion. Middle and lower slope carbonates are generally rich in fossil shells of chemosynthetic organisms. Mg calcite pelloidal matrix and acicular to botryoidal aragonitic void-filling cements are common petrographic features of these hydrocarbon-derived carbonates. At two sites carbonates are mixed with barite.

Roberts, H. H., P. Aharon, et al. (1990). "SEA-FLOOR RESPONSES TO HYDROCARBON SEEPS, LOUISIANA CONTINENTAL-SLOPE." Geo-Marine Letters **10**(4): 232-243.

Observations and samples from research submersible dives confirm that brines, crude oil, fluid mud, and gases are common seep products. Through this mechanism a unique interplay of geochemical, geologic, and biological processes resulting in unusual sea floor features ranging from carbonate-rich nodular sediments to mounds with tens of meters relief. Stable carbon isotopes occluded in the carbonates provide a permanent imprint that links these authigenic carbonates to by-products of microbial breakdown of crude oil and gas. Recent DS-FOR-ALL ALVIN dives confirm that hydrocarbon seeps and their accompanying chemosynthetic communities and authigenic carbonate mounds occur over the entire depth range of the slope.

Rooker, J. R., J. P. Turner, et al. (2006). "Trophic ecology of Sargassum-associated fishes in the Gulf of Mexico determined from stable isotopes and fatty acids." Marine Ecology-Progress Series **313**: 249-259.

Natural dietary markers (stable isotopes and fatty acids) were used to determine the trophic structure and characterize carbon source(s) of juvenile and adult fishes associated with floating Sargassum in mid-shelf waters of the Gulf of Mexico. Stable carbon isotope ratios ($\delta^{13}\text{C}$) of 4 autotrophs (Cladophora sp., phytoplankton [based on particulate organic matter, POM], *S. fluitans*, *S. natans*) were distinct (range -16.3 to -21.0 parts per thousand), with *S. fluitans* and *S. natans* enriched by 2 to 5 parts per thousand relative to *Cladophora* sp.

and POM. Stable nitrogen isotope ratios ($\delta N-15$) of both *S. fluitans* and *S. natans* were depleted by 5 to 7 parts per thousand compared to *Cladophora* sp. and POM. The majority of VC values of consumers were between -16 and -18 parts per thousand, and VC values were most depleted for juvenile shrimps, juvenile crabs and certain juvenile fishes (e.g. *Aluterus heudeloti*, *Monacanthus hispidus*, *Abudefduf saxatilis*, *Histrio histrio*, *Seriola dumerih*). Stable carbon isotope ratios of adult fishes varied from -16.1 to -17.5 parts per thousand. Enrichment of $\delta N-15$ occurred with increasing trophic position, and the lowest values were observed for juvenile crustaceans, which ranged from 6.0 to 8.7 parts per thousand. The majority of juvenile fishes were secondary heterotrophs ($\delta N-15$ values ca. 8.0 to 11.0 parts per thousand), while most adult fishes were tertiary consumers with $\delta N-15$ values ranging from 11.9 to 14.3 parts per thousand. Carbon source estimates from a 2-source mixing model indicated that the 78% of organic matter supplied to consumers (pooled across taxa) in the Sargassum complex was derived from POM. Fatty acid signatures of the primary producers were significantly different, and were used to further evaluate organic matter contribution to Sargassum-associated consumers. C-22 polyunsaturated fatty acids (PUFAs) (22:6n-3, 22:5n-3) were most abundant in POM, while high levels of C-18 and C-20 PUFAs were observed for *Cladophora* sp. and *Sargassum* spp. (18:2n-6 and 20:4n-6, respectively). Consumer signatures were dominated by 22:6n-3, and principal component analysis indicated that fatty acid signatures of each of the 6 juvenile and 6 adult fish species were highly similar to POM and distinct from the other producers within the Sargassum complex.

Rostad, C. E., W. E. Pereira, et al. (1999). "Distribution and transport of selected anthropogenic lipophilic organic compounds associated with Mississippi River suspended sediment, 1989-1990." Archives of Environmental Contamination and Toxicology **36**(3): 248-255.

In the first study on this scale, distribution and transport of selected hydrophobic halogenated organic compounds associated with suspended sediment from the lower Mississippi River and its principal tributaries were determined during two spring and two summer cruises. Lipophilic organic compounds identified on the suspended sediment included hexachlorobenzene, pentachlorobenzene, pentachloroanisole, dacthal, chlordane (cis- and trans-), nonachlor (trans-), chlorthalonil, and penta-, hexa-, hepta-, and octachlorobiphenyls. Most of these compounds come from nonpoint sources. Mass loadings of most of the compounds increased from upstream to downstream on the main stem of the Mississippi River. Of the tributaries studied, the Ohio River had the most significant effect on contaminant loads. Suspended sediment transport to the Gulf of Mexico of the most abundant, widely distributed compound class, PCBs, was estimated at 6,750 kg per year.

Rowe, G. T. (2001). "Seasonal hypoxia in the bottom water off the Mississippi River delta." Journal of Environmental Quality **30**(2): 281-290.

Hypoxia (oxygen concentration less than 2 mg L⁻¹ or 62.5 $\mu\text{mol m}^{-3}$) occurs on

the Louisiana continental shelf during summer when the consumption of oxygen by sediment and water column respiration exceed resupply by photosynthesis and mixing. Biological processes that consume or produce oxygen have been summarized in a budget that can be used to quantify the degree to which consumption in deep water and in the sediments exceeds net production and thus the time it takes to reach hypoxic conditions following the spring onset of stratification. The net consumption rate by the sea floor biota (sediment oxygen consumption, SOC) is inversely related to oxygen concentration and directly related to temperature. Photosynthesis is of potential importance throughout the deep water column and on the sea floor when light is adequate. A non-steady state, time-dependent numerical simulation model is used to compare biological and physical processes with shipboard measurements and continuous near bottom records. The simulations illustrate possible variations in oxygen concentration on time scales of hours to months, and these in general match much of the variability in the direct observations at time scales of days to weeks. The frequently observed unremitting anoxia lasting weeks at some locations is not produced in the present simulations. A possible explanation is the chemical oxidation in the water column of reduced metabolic end-products produced in the sediments by anaerobic metabolism. Direct measurements of biological processes could lead to better understanding of how extrinsic forcing functions can best be managed to improve water quality.

Rowe, G. T., M. E. C. Kaegi, et al. (2002). "Sediment community metabolism associated with continental shelf hypoxia, Northern Gulf of Mexico." Estuaries **25**(6A): 1097-1106. Net fluxes of respiratory metabolites (O₂, dissolved inorganic carbon (DIC), NH₄⁺, NO₃⁻, and NO₂⁻) across the sediment-water interface were measured using in-situ benthic incubation chambers in the area of intermittent seasonal hypoxia associated with the Mississippi River plume. Sulfate reduction was measured in sediments incubated with trace-levels of S-35-labeled sulfate. Heterotrophic remineralization, measured as nutrient regeneration, sediment community oxygen consumption (SOC), sulfate reduction, or DIC production, varied positively as a function of temperature. SOC was inversely related to oxygen concentration of the bottom water. The DIC fluxes were more than 2 times higher than SOC alone, under hypoxic conditions, suggesting that oxygen uptake alone cannot be used to estimate total community remineralization under conditions of low oxygen concentration in the water column. A carbon budget is constructed that compares sources, stocks, transformations, and sinks of carbon in the top meter of sediment. A comparison of remineralization processes within the sediments implicates sulfate reduction as most important, followed by aerobic respiration and denitrification. Bacteria accounted for more than 90% of the total community biomass, compared to the metazoan invertebrates, due presumably to hypoxic stress.

Russell, M. J. and P. A. Montagna (2007). "Spatial and temporal variability and drivers of net ecosystem metabolism in western Gulf of Mexico estuaries." Estuaries and Coasts **30**(1): 137-153.

Net ecosystem metabolism (NEM) is becoming a commonly used ecological indicator of estuarine ecosystem metabolic rates. Estuarine ecosystem processes are spatially and temporally variable, but the corresponding variability in NEM has not been properly assessed. Spatial and temporal variability in NEM was assessed in four western Gulf of Mexico shallow water estuaries. NEM was calculated from high-frequency dissolved oxygen measurements. Interbay, intrabay, and water column spatial scales were assessed for NEM, gross primary production (GPP), and respiration (R) rate variability. Seasonal, monthly, and daily temporal scales in NEM, GPP, and R were also assessed. Environmental conditions were then compared to NEM to determine which factors were correlated with each temporal and spatial scale. There was significant NEM spatial variability on interbay, intrabay, and water column spatial scales. Significant spatial variability was ephemeral, so it was difficult to ascertain which environmental conditions were most influential at each spatial scale. Significant temporal variability in NEM on seasonal, monthly, and daily scales was found and it was correlated to temperature, salinity, and freshwater inflow, respectively. NEM correlated strongly with dissolved oxygen, temperature, and salinity, but the relationships were different in each bay. The dynamics of NEM on daily scales indicate that freshwater inflow events may be the main driver of NEM in the semiarid estuaries studied. The variable nature of NEM found here is further evidence that it is not valid to use single station monitoring deployments for assessment of whole estuarine ecosystem metabolic rates in large ecosystems. The relationship between NEM and temperature, salinity, and freshwater inflow events could drive predictive models assessing the potential influence of projected climate change and watershed development scenarios on estuarine metabolic rates.

Ruttenberg, K. C. and M. A. Goni (1997). "Phosphorus distribution, C:N:P ratios, and $\delta^{13}\text{C}(\text{oc})$ in arctic, temperate, and tropical coastal sediments: Tools for characterizing bulk sedimentary organic matter." *Marine Geology* **139**(1-4): 123-145. Onshore-offshore trends in phosphorus (P), organic carbon (OC), and total nitrogen (TN) concentration, P distribution, elemental organic C:N:P ratios, and stable carbon isotopic composition of OC ($\delta^{13}\text{C}(\text{OC})$) of surficial sediments, are presented from three river-dominated coastal regimes: the Mackenzie River/Beaufort shelf in the Canadian Arctic; the Mississippi Delta and Louisiana shelf in the temperate Gulf of Mexico; and the tropical Amazon shelf. These parameters, measured in surficial sediments from the three sites, are used to assess changes in the importance of terrestrial and marine organic matter sources to sediments as a function of distance from the locus of riverine discharge. Trends in elemental ratio data from the Arctic transect, and a portion of the Gulf of Mexico transects, can be explained in terms of a two-end-member mixture of terrestrial and marine phytodetritus. In the arctic transect, covariation of organic C:P ratios with $\delta^{13}\text{C}(\text{OC})$ is consistent with a two-end-member mixture of terrestrial and marine organic matter. A similar relationship between C:P ratios and $\delta^{13}\text{C}(\text{OC})$ is not evident in Gulf of Mexico or Amazon shelf sediments. At these sites the two-end-member model fails to explain the data

adequately. The most striking feature of the onshore-offshore trends in elemental OC:OP and OC:TN ratios is the occurrence of low ratios in sediments from deep-water stations in the Gulf of Mexico and all stations on the Amazon shelf, resulting from P and N enrichments exceeding the Redfield Ratio for marine plankton. Three explanations are discussed to account for these low ratios: (1) the dominance of refractory OP- and ON-compounds in the residuum of degraded organic matter; (2) differential sorption of OP- and N-compounds, regardless of lability, on the surfaces of the fine-grained sediments characteristic of these sites; and (3) a dominance of bacterial biomass, or components derived from bacterial biomass. Elemental ratios and $\delta(13)C(OC)$ signatures indicate that differential sorption may be most important in the deep-water Gulf of Mexico sites. In contrast, elemental ratios and $\delta(13)C(OC)$, on the Amazon shelf are most consistent with a sedimentary organic matter pool dominated by bacterial biomass, or derivative substances. (C) 1997 Elsevier Science B.V.

Santschi, P. H., L. Guo, et al. (1999). "Boundary exchange and scavenging of radionuclides in continental margin waters of the Middle Atlantic Bight: implications for organic carbon fluxes." Continental Shelf Research **19**(5): 609-636.

Continental margins are sites where energy dissipation from physical (e.g., waves currents and tides) and biochemical process (e.g., rates of photosynthesis and decomposition) are highest. As a consequence, continental margins have been considered as possibly important sites of organic matter production and export to the ocean interior. As part of the Ocean Margins Program, vertical profiles of Th-234, Pb-210, particulate organic carbon, suspended particulate matter concentrations, vertical fluxes of sinking particles and associated natural radionuclides (e.g., Th-234, Pb-210, C-14), and elemental composition (e.g., C, N) were measured. Boundary scavenging and exchange processes of natural radionuclides and organic matter were investigated across the continental margin in the Middle Atlantic Eight (MAE). Large deficiencies of Th-214 with respect to production from U-238 decay in the MAB down to 2300 m water depth imply rapid benthic nepheloid layer exchange processes not only in deeper water, but also in the upper water column of the continental slope. Calculated lateral fluxes of organic carbon, likely of episodic nature and related to the relative position of the Gulf Stream, are up to an order of magnitude larger than long-term vertical deposition rates in the sediments. (C) 1999 Elsevier Science Ltd. All rights reserved.

Santschi, P. H., L. D. Guo, et al. (1995). "ISOTOPIC EVIDENCE FOR THE CONTEMPORARY ORIGIN OF HIGH-MOLECULAR-WEIGHT ORGANIC-MATTER IN OCEANIC ENVIRONMENTS." Geochimica Et Cosmochimica Acta **59**(3): 625-631.

Previous work has suggested that apparent old C-14 ages for oceanic DOC are the result of mixing of different organic carbon fractions. This report provides direct evidence for a contemporary C-14 age of a high-molecular-weight (HMW) fraction of colloidal organic carbon (greater than or equal to 10 kD). Colloidal organic matter, COM(10) (from 10 kDaltons (kD) to 0.2 μ m), isolated from the upper water column of the Gulf of Mexico and the Middle Atlantic Bight (MAB)

region, generally has a contemporary age (i.e., younger than a few decades), while COM(1) (from 1 kD to 0.2 μ m), is apparently old: 380-4500 y BP. Thus, HMW COM(10) (3-5% of DOC) from the upper water column is derived from living particulate organic matter (POM) and cycles rapidly, while a significant fraction of low-molecular-weight (less than or equal to 1 kD) DOM is likely more refractory, and cycles on much longer time scales. The presence of pigment biomarker compounds in COM(1) from the upper water column points to selected phytoplankton species as one of the sources of COM. Terrestrial carbon as another source of COM is suggested from the inverse correlation between $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values, as well as the increasing $\delta^{13}\text{C}$ values with increasing salinity. Th-234-derived turnover times of COM(10) and COM(1) from both the Gulf of Mexico and MAB are consistently short, 1-20 and 3-30 days, respectively. These short residence times support the hypothesis that C-14 ages of colloidal fractions of DOC are the result of COM fractions being a mixture of several endmembers with fast and slow turnover rates.

Santschi, P. H., S. D. Oktay, et al. (2007). "Carbon isotopes and iodine concentrations in a Mississippi River delta core recording land use, sediment transport, and dam building in the river's drainage basin." Marine Environmental Research **63**(3): 278-290. Sedimentary material from coastal and nearshore areas in the Mississippi Delta region are comprised of different organic carbon sources with diverse ages that require isotopic and elemental records for resolving the various sources of plant residues. Carbon isotopic (C-13 , C-14) values were used to differentiate contributions from plants using the C_3 , C_4 , and/or CAM (crassulaccean acid metabolism) carbon fixation pathways., and iodine concentrations indicated that wetland plant residues are a significant source of organic carbon in a sediment core from the Mississippi River delta region collected at a 60 m water depth. This sediment core had been extensively described in Oktay et al. [Oktay, S.D., Santschi, P.H., Moran, J.E., Sharma, P., 2000. The 129 Iodine Bomb Pulse Recorded in Mississippi River delta Sediments: Results from Isotopes of ^1I , $^{\text{Pu}}$, $^{\text{Cs}}$, $^{\text{Pb}}$, and $^{\text{C}}$. *Geochim. Cosmochim. Acta* 64 (6), 989-996.] and significantly, includes unique features that had not previously been seen in the marine environment. These special features include a plutonium isotopic close-in fallout record that indicates a purely terrestrial source for these sediment particles and the elements associated with it, and a distinct iodine isotopic peak (as well as peaks for plutonium and cesium isotopes) that indicate little bioturbation in this core. Our carbon isotopic and iodine data can thus be compared to published records of changes in drainage basin land use, river hydrology, and hydrodynamic sorting of suspended particles to elucidate if these changes are reflected in nearshore sediments. This comparison suggests a significant contribution for organic carbon (OC) from C_4 plants to these sediments during the 1950's to early 1960's. Relative older carbon isotopes, and episodically high iodine concentrations (up to 34 ppm) were observed during this time period that (1) indicate sediment deposition that is coincident with the times of major hydrological changes induced from dam and levee building in both the upper and lower reaches of the Mississippi River drainage basin, and (2) suggest episodic

organic carbon deposition from wetland plant residues. (c) 2006 Elsevier Ltd. All rights reserved.

Sassen, R., S. Joye, et al. (1999). "Thermogenic gas hydrates and hydrocarbon gases in complex chemosynthetic communities, Gulf of Mexico continental slope." Organic Geochemistry **30**(7): 485-497.

Where abundant at the sea floor, thermogenic gas hydrates impact bacterially-mediated processes in chemosynthetic communities dependent on methane and H₂S. Our main gas hydrate sites are at similar to 540 m water depth and relatively low temperature (similar to 7 degrees C). Gas hydrates outcrop as vein-fillings in hemipelagic muds near gas vents within chemosynthetic communities. Molecular and isotopic properties of hydrate-forming C-1-C-5 hydrocarbons and CO₂ provide insight to bacterially-mediated processes. Hydrate-bound methane is altered by bacterial oxidation, as indicated by enrichment of C-13 and deuterium (D), and by CO₂ depleted in C-13. The degree of gas hydrate alteration appears related to duration of exposure at the sea floor. In hydrate-associated sediments, bacterial oxidation of a mixed pool of hydrocarbons yields a net production of CO₂ depleted in C-13. Bacterial oxidation of hydrate-bound methane and free hydrocarbon gases in adjacent sediments could contribute to gas hydrate decomposition. Some thermogenic carbon in sediments could be recycled via methanogenesis to yield a net production of bacterial methane depleted in C-13. Our results strengthen the hypothesis that gas hydrates could favor life in other extreme environments at low temperatures. (C) 1999 Elsevier Science Ltd. All rights reserved.

Sassen, R., S. L. Losh, et al. (2001). "Massive vein-filling gas hydrate: relation to ongoing gas migration from the deep subsurface in the Gulf of Mexico." Marine and Petroleum Geology **18**(5): 551-560.

A gas hydrate mound that contains massive, vein-filling, structure II gas hydrate occurs on the upper continental slope (similar to 540 m water depth) of the Gulf of Mexico, southwest of the Mississippi Delta. The mound is located in the Green Canyon (GC) Block 185, adjacent to Jolliet Field in GC 184. Jolliet Field contains oil and gas that filled fault traps caused by salt deformation during late Pleistocene-Holocene time. In contrast to reservoir oil in Jolliet Field, which shows bacterial oxidation effects, the C-1-C-5 reservoir gas is unaltered by bacterial oxidation. Disassociated gas is assumed to have recently entered from the subsurface hydrocarbon system. Vertical migration of gas along faults is ongoing, manifested on the sea floor by gas vents, gas hydrate, complex chemosynthetic communities, and by a large gas plume that extends from the vents to the sea surface. The isotopic properties of C-1-C-5 hydrocarbons from reservoirs, gas vents, and gas hydrate correlate closely. Although outcropping gas hydrate is transiently stable because of variations in seawater temperature, the bulk of buried gas hydrate at GC 185 is stable and perhaps increasing in volume because of the copious gas flux. The massive accumulation of gas hydrate at the GC 185 site is attributed to the gas that has recently entered the

vents, largely from Jolliet Field, and to the synchronous activation of fault conduits allowing gas migration to the sea floor. Synchronous late gas charge and faulting could also explain the wide distribution of gas hydrate across the upper Gulf slope. (C) 2001 Elsevier Science Ltd. All rights reserved.

Sassen, R., I. R. MacDonald, et al. (1998). "Bacterial methane oxidation in sea-floor gas hydrate: Significance to life in extreme environments." Geology **26**(9): 851-854.

Samples of thermogenic hydrocarbon gases, from vents and gas hydrate mounds within a sea-floor chemosynthetic community on the Gulf of Mexico continental slope at about 540 m depth, were collected by research submersible. Our study area is characterized by low water temperature (mean = 7 degrees C), high pressure (about 5400 kPa), and abundant structure II gas hydrate. Bacterial oxidation of hydrate-bound methane (CH₄) is indicated by three isotopic properties of gas hydrate samples. Relative to the vent gas from which the gas hydrate formed, (1) methane-bound methane is enriched in C-13 by as much as 3.8 parts per thousand PDB (Peedee belemnite), (2) hydrate-bound methane is enriched in deuterium (D) by as much as 37 parts per thousand SMOW (standard mean ocean water), and (3) hydrate-bound carbon dioxide (CO₂) is depleted in C-13 by as much as 22.4 parts per thousand PDB. Hydrate-associated authigenic carbonate rock is also depleted in C-13. Bacterial oxidation of methane is a driving force in chemosynthetic communities, and in the concomitant precipitation of authigenic carbonate rock that modifies sea-floor geology. Bacterial oxidation of hydrate-bound methane expands the potential boundaries of life in extreme environments.

Sassen, R., A. V. Milkov, et al. (2003). "Gas venting and subsurface charge in the Green Canyon area, Gulf of Mexico continental slope: evidence of a deep bacterial methane source?" Organic Geochemistry **34**(10): 1455-1464.

Questions as to the role of modern carbon in methanogenesis and the maximum depth of methane sources in the Gulf of Mexico continental slope remain unanswered. A research submersible was used to sample mixed bacterial and thermal gas ($\delta^{13}\text{C}$ of methane = -62.8 parts per thousand, δD = -176 parts per thousand) venting to the water column from the Gulf slope in Green Canyon (GC) 286. The $\Delta^{14}\text{C}$ value of the methane (-998 parts per thousand) is consistent with fossil carbon. Another gas vent on GC 185 is 100% methane ($\delta^{13}\text{C}$ = -62.9 parts per thousand, δD = -155 parts per thousand) and may be from a bacterial source. The $\Delta^{14}\text{C}$ (-997 parts per thousand) of this bacterial methane is also consistent with fossil carbon. Fossil bacterial methane and thermal hydrocarbons are present in Pliocene to Pleistocene reservoirs (similar to 3509-4184 m) of Genesis Field (GC 205, 161, 160). Oil in these reservoirs is biodegraded but gas is not, suggesting that gas charge to reservoirs continues presently at 3-4 km depth. Mixed thermal and bacterial methane may charge the deep reservoirs, and fossil methane from depth may ultimately vent on the sea floor at GC 286 and GC 185. Results of this study of Green Canyon suggest that bacterial methane in gas vents and in reservoirs is from deep fossil sources. (C) 2003 Elsevier Ltd. All rights reserved.

Sassen, R., H. H. Roberts, et al. (1993). "CHEMOSYNTHETIC BACTERIAL MATS AT COLD HYDROCARBON SEEPS, GULF OF MEXICO CONTINENTAL-SLOPE." Organic Geochemistry **20**(1): 77-&.

White and pigmented filamentous bacterial mats dominated by several undescribed species of *Beggiatoa* were sampled during research submersible dives to cold hydrocarbon seep sites on the upper continental slope off Louisiana (130-550 m). Mats occur at the interface between reducing sediments and the oxygenated water column. They are localized at sea floor features related to seepage of biogenic methane and crude oil, but there is little evidence that the organisms utilize the hydrocarbons directly. Granules of elemental sulfur (S₀) are visible within cells of *Beggiatoa*, and mat material is characterized by high contents of S₀ (up to 193,940 ppm). The *Beggiatoa* biomass is isotopically light ($\delta^{13}\text{C} = -27.9$ parts per thousand PDB). Our geochemical data suggest that the *Beggiatoa* species are part of a complex bacterial assemblage in cold seep sediments. They oxidize H₂S derived from the bacterial sulfate reduction that accompanies bacterial hydrocarbon oxidation when O₂ is depleted in sediments, and fix isotopically light carbon from CO₂ that is the result of bacterial hydrocarbon oxidation. *Beggiatoa* mats appear to retard loss of hydrocarbons to the water column by physically retaining fluids in sediments, a function that could enhance production by other bacteria of the H₂S and CO₂ needed by *Beggiatoa*.

Sassen, R., H. H. Roberts, et al. (2004). "Free hydrocarbon gas, gas hydrate, and authigenic minerals in chemosynthetic communities of the northern Gulf of Mexico continental slope: relation to microbial processes." Chemical Geology **205**(3-4): 195-217.

Research submersibles and piston cores were used to sample two chemosynthetic communities in the Gulf of Mexico continental slope at similar to 540 m water depth. Vent gas from the deep subsurface is the starting material from which other carbon pools are derived, including gas hydrate, free hydrocarbon gas in sediment, and authigenic carbonate rock. Gas crystallizes as exposed mounds of structure II gas hydrate and as massive vein-fillings in hemipelagic mud. Venting rates from gas hydrate mounds periodically increase after the temperature of the bottom water increases. Gas hydrate decomposition is largely restricted to exposed hydrate and at shallow depth in sediment. Overall, gas hydrate is accumulating, not decomposing at study sites. Most free gas in sediment appears to be destroyed in situ by anaerobic microbial oxidation in chemosynthetic communities, leading to sequestration of carbon as abundant authigenic carbonate rock depleted in C-13. Free methane is rapidly oxidized leaving residual methane enriched in C-13. Some in situ microbial CO₂ reduction occurs, and methane depleted in C-13 mixes with vent methane enriched in C-13. The C-2-C-5 hydrocarbons of vent gas initially most depleted in C-13 (ethane, isobutane, isopentane) are least affected by microbial oxidation, whereas hydrocarbons initially enriched in C-13 (propane, normal butane, normal pentane) are most affected. Anaerobic microbial oxidation of all C-1-C-5 hydrocarbon gases, not only methane, may be significant in chemosynthetic

communities. Microbial processes contribute to the development and stability of chemosynthetic communities by providing required H₂S. Anaerobic microbial processes lead to deposition of diagnostic authigenic minerals related to the carbon (carbonate minerals) and sulfur cycles (pyrite, elemental sulfur), altering the seafloor. Seafloor cementation favors fauna such as chemosynthetic tubeworms and seep mussels by forming carbonate hardgrounds on an otherwise unfavorable mud-dominated seafloor. (C) 2004 Elsevier B.V. All rights reserved.

Schnitzer, A. and D. K. Steinberg (2002). "Natural diets of vertically migrating zooplankton in the Sargasso Sea." *Marine Biology* **141**(1): 89-99.

The feeding preferences of three common diel vertically migrating zooplankton were investigated from December 1999 to October 2000 at the U.S. JGOFS Bermuda Atlantic Time-Series Study (BATS) station in the Sargasso Sea. Gut content analysis of the copepods *Pleuromamma xiphioides* (Giesbrecht) and *Euchirella messinensis* (Claus) and of the euphausiid *Thysanopoda aequalis* (Hansen) indicated that all three species fed on a wide variety of phytoplankton, zooplankton, and detrital material. Diet changes generally reflected seasonal trends in phytoplankton community structure. However, species-specific feeding preferences and differences in feeding selectivity among the three species were evident, and in general agreement with feeding habits predicted from the analysis of mouthpart morphology. The euphausiid *T. aequalis* fed equally on more different food types compared to both copepod species. The copepod *P. xiphioides* consumed a diverse assemblage of phytoplankton from late winter through the summer (78-93% of gut items, by number, were phytoplankton) and based its diet more strongly on carnivorous feeding in autumn and early winter (31% and 61% of gut items were phytoplankton, respectively). *E. messinensis* showed the greatest feeding specialization, with a strong preference for pennate diatoms in winter and spring and for coccolithophorids during late summer and fall (constituting 67-93% of gut items by number). All three species consumed diatoms more than other phytoplankton taxa, even though diatoms form only a small fraction of the phytoplankton biomass in the Sargasso Sea. Although the majority of gut items identified were phytoplankton cells, the relative biomass contribution of these small cells may be lower than that of zooplankton and detritus. Zooplankton on which the three species primarily preyed were protozoans and crustaceans, but also included other metazoans such as chaetognaths and cnidarians. Marine snow was also an important component of the diet in all three species, with typically > 50% and rarely < 20% of the gut content being olive-green debris. Marine snow from larvacean houses was found in the guts of all three species, while *E. messinensis* appeared to selectively consume marine snow aggregates enriched with bicapitate *Nitzschia* spp. Large cyanobacteria (>4 µm in diameter) found in guts were also likely consumed with marine snow. The species-specific differences in the diets of these three migrating species suggest that an individual species approach is important in determining how feeding habits affect the structure of pelagic food webs and carbon cycling in the sea. Electronic supplementary material to this paper can be

obtained by using the Springer LINK server located at <http://dx.doi.org/10.1007/s00227-002-0815-8>.

Sengupta, B. K. and P. Aharon (1994). "BENTHIC FORAMINIFERA OF BATHYAL HYDROCARBON VENTS OF THE GULF-OF-MEXICO - INITIAL REPORT ON COMMUNITIES AND STABLE ISOTOPES." Geo-Marine Letters **14**(2-3): 88-96.

Substrates associated with active hydrocarbon vents in bathyal Gulf of Mexico support numerous foraminiferal species, with a few of them showing unusually high relative abundances. In the 584- to 695-m-depth range, *Bolivina ordinaria*, *Gavelinopsis translucens*, and *Cassidulina neocarinata* strongly dominate the vent community, whereas *Bolivina subaenariensis* and *Uvigerina laevis* play this role around a vent at 216 m water depth. The bathymetric imprint on the foraminiferal record is also seen in the $\delta(18)O$ compositions of some species, including *Uvigerina peregrina*. The adaptation of foraminiferal communities to bacterial (*Beggiatoa*) mats, in which the redox boundary is very close to the sediment-water interface, and anomalous depletions of C-13 in *U. peregrina* (relative to the same species from nonventing sites) indicate that several species are probably facultative anaerobes and tolerant of H₂S toxicity.

SenGupta, B. K., E. Platon, et al. (1997). "Foraminiferal colonization of hydrocarbon-seep bacterial mats and underlying sediment, Gulf of Mexico slope." Journal of Foraminiferal Research **27**(4): 292-300.

Around bathyal hydrocarbon seeps of Green Canyon, Gulf of Mexico, a community of foraminifera has colonized mats of *Beggiatoa*, a chemolithotrophic, sulfide-oxidizing bacterium. The O₂-H₂S boundary zone in these mats is likely to be within 1-2 mm of the sediment-water interface. Judging by Rose-Bengal staining, small populations of some foraminiferal species survive under the *Beggiatoa* mats, down to a substrate depth of at least 2 or 3 cm, where the sediment is black and the pore fluid is sulfidic. These species, including *Bolivina albatrossi*, *Bolivina ordinaria*, *Cassidulina neocarinata*, *Gavelinopsis translucens*, *Osangularia rugosa*, and *Trifarina bradyi*, are microaerophiles or facultative anaerobes. The subsurface distributions and densities of *Bolivina albatrossi* suggest that it is the most tolerant of anoxia and sulfide toxicity. Transmission electron microscopy of 12 individuals of diverse species failed to confirm the presence of live foraminifera under the bacterial mats. The cytoplasm, when present, was degraded, although the structure of some organelles suggests that some of the individuals had died only recently. Initial stable-isotope analyses of empty tests of three species (*Uvigerina peregrina*, *Bolivina subaenariensis*, and *Lenticulina* sp.) from previously studied seep sites show anomalously negative and wide-ranging $\delta(13)C$ values (-1.3 parts per thousand to -3.6 parts per thousand PDB) that are typical of seep CO₂ plumes, but not of associated sediment-pore fluids. However, the carbon-isotopic signature in the dominant species (especially in *Bolivina albatrossi*) living under *Beggiatoa* mats in deep-bathyal Green Canyon is presently unknown. Thus, whether species of foraminifera invading the anoxic layers under *Beggiatoa* mats can construct tests in these microhabitats remains unresolved.

Severinghaus, J. P., W. S. Broecker, et al. (1996). "Transect along 24 degrees N latitude of C-14 in dissolved inorganic carbon in the subtropical North Atlantic Ocean." Radiocarbon **38**(3): 407-414.

The distribution of bomb-produced C-14 in the ocean provides a powerful constraint for circulation models of upper ocean mixing. We report C-14 measurements from an east-west section of the main thermocline at 24 degrees N latitude in the subtropical North Atlantic Ocean in summer 1992, and one profile from the Gulf of Mexico in 1993. Observed gradients reflect the transient invasion of bomb C-14 into the thermocline via mixing along isopycnals from the poleward outcrop, with progressively more sluggish mixing at greater depths. A slight deepening of the profile is observed over the 20-yr period since the GEOSECS survey at one location where the comparison is possible.

Sheu, D. D. and B. J. Presley (1986). "VARIATIONS OF CALCIUM-CARBONATE, ORGANIC-CARBON AND IRON SULFIDES IN ANOXIC SEDIMENT FROM THE ORCA BASIN, GULF OF MEXICO." Marine Geology **70**(1-2): 103-118.

Skoog, A., B. Biddanda, et al. (1999). "Bacterial utilization of dissolved glucose in the upper water column of the Gulf of Mexico." Limnology and Oceanography **44**(7): 1625-1633.

Several aspects of bacterial glucose assimilation and bacterial production (EP) were investigated over 2 d in the upper 300 m of the Gulf of Mexico. Glucose concentrations ranged from 2 to 15 nM in surface seawater; glucose utilization rates were 1-3 nM d(-1) in the upper 150 m of the water column and 0.02-0.8 nM d(-1) in deeper water (150-300 m). Turnover of glucose and bacteria were similar and were in the range of 0.01-0.4 d(-1). Measured glucose assimilation rates imply that glucose supports similar to 5-10% of the observed BP in surface waters. The limiting factors for bacterial glucose utilization varied with depth. Glucose assimilation seemed to be limited by availability of inorganic N in the chlorophyll maximum. Additions of nitrate or ammonium had similar effects on glucose assimilation. BP was limited by C below and above the chlorophyll maximum. Additions of high-molecular-weight (HMW) dissolved organic matter (DOM) decreased bacterial glucose uptake rates, indicating that substances competing with glucose assimilation were derived from HMW DOM extracellularly. Thus, the measurement of free glucose assimilation appears to integrate bacterial utilization of combined glucose and indicates that many of the free sugars in seawater may be derived from polymers. The higher glucose assimilation rates achieved with inorganic nutrient additions indicate that bacterial degradation of C-rich organic matter (OM) could vary between ocean regions with varying inorganic nutrient concentrations.

Slomp, C. P. and P. Van Cappellen (2004). "Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact." Journal of Hydrology **295**(1-4): 64-86.

Nutrient input through submarine groundwater discharge (SGD) rivals river inputs

in certain regions and may play a significant role in nutrient cycling and primary productivity in the coastal ocean. In this paper, we review the key factors determining the fluxes of nitrogen (N) and phosphorus (P) associated with SGD and present a compilation of measured rates. We show that, in particular, the water residence time and the redox conditions in coastal aquifers and sediments determine fluxes and ratios of N and P in SGD. In many coastal groundwater systems, and especially in contaminated aquifers, N/P ratios exceed those in river water and are higher than the Redfield ratio. Thus, anthropogenically driven increases in SGD of nutrients have the potential to drive the N-limited coastal primary production to P-limitation. River input of N and P to the coastal ocean has doubled over the past 50 yr. Results of a dynamic biogeochemical model for the C, N and P cycles of the global proximal coastal ocean (which includes large bays, the open water part of estuaries, deltas, inland seas and salt marshes), suggest that this has led to a factor 2 increase in primary production and biomass and a decline in water column N/P ratios i.e. the system has become more N-limiting. With the same model, we show that an increase of SGD-N fluxes to similar to 0.7-1.1 Tmol yr⁻¹ (with a SGD N/P ratio of 100; equal to similar to 45-70% of pre-human riverine N-inputs) is required to drive the coastal ocean to P-limitation within the next 50 yr. (C) 2004 Elsevier B.V. All rights reserved.

Smith, E. B., K. M. Scott, et al. (2000). "Growth and condition of seep mussels (*Bathymodiolus childressi*) at a Gulf of Mexico Brine Pool." *Ecology* **81**(9): 2392-2403. The banks of Brine Pool NR1, a brine-filled pockmark in the Gulf of Mexico, are host to a population of *Bathymodiolus childressi*, a hydrocarbon seep mussel with methanotrophic endosymbionts. The mussel community surrounds the pool, covering an area of similar to 540 m² and can be divided into two distinct zones separated by a transitional area. The inner zone extends inward from the edge of the pool similar to 1 m. The water among the mussels in this zone has high methane concentrations (>200 $\mu\text{mol/L}$) and moderate oxygen concentrations (nondetectable to 161 $\mu\text{mol/L}$). Hydrogen sulfide was rarely detected in this zone. The outer zone extends similar to 1 m inward from the outer edge of the mussel bed. This zone also has high methane concentrations in the water among the mussels (>200 $\mu\text{mol/L}$), but lower average oxygen levels and areas with very high levels of hydrogen sulfide. The two zones are linked with a transitional area, the middle zone, ranging in width from 1 to 4 m, where intermediate environmental conditions are found. The inner zone was relatively homogenous, while spatial heterogeneity was high in the middle and outer zones, both in the characteristics of the mussel population and in their environment. Size-frequency distributions indicate that the inner zone is an area of active recruitment, with very little recruitment occurring in either the middle or outer zones. Physiological condition indices of the mussels were significantly higher in the inner zone than in the outer zone in some years. Comparisons of growth parameters also indicate better growth conditions in the inner zone. Physiological condition and growth did not change between the first two years of the study. However, a significant change in both was detected between 1994 and 1995, suggesting that this

deep-sea community is exposed to an unexpected temporal variability in environmental conditions.

Smith, V. H., G. D. Tilman, et al. (1999). "Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems." Environmental Pollution **100**(1-3): 179-196.

In the mid-1800s, the agricultural chemist Justus von Liebig demonstrated strong positive relationships between soil nutrient supplies and the growth yields of terrestrial plants, and it has since been found that freshwater and marine plants are equally responsive to nutrient inputs. Anthropogenic inputs of nutrients to the Earth's surface and atmosphere have increased greatly during the past two centuries. This nutrient enrichment, or eutrophication, can lead to highly undesirable changes in ecosystem structure and function, however. In this paper we briefly review the process, the impacts, and the potential management of cultural eutrophication in freshwater, marine, and terrestrial ecosystems. We present two brief case studies (one freshwater and one marine) demonstrating that nutrient loading restriction is the essential cornerstone of aquatic eutrophication control. In addition, we present results of a preliminary statistical analysis that is consistent with the hypothesis that anthropogenic emissions of oxidized nitrogen could be influencing atmospheric levels of carbon dioxide via nitrogen stimulation of global primary production. (C) 1999 Elsevier Science Ltd. All rights reserved.

Sorooshian, A., N. L. Ng, et al. (2007). "Particulate organic acids and overall water-soluble aerosol composition measurements from the 2006 Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS)." Journal of Geophysical Research-Atmospheres **112**(D13).

[1] The Center for Interdisciplinary Remotely-Piloted Aircraft Studies (CIRPAS) Twin Otter participated in the Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS) mission during August-September 2006. A particle-into-liquid sampler (PILS) coupled to ion chromatography was used to characterize the water-soluble ion composition of aerosol and cloud droplet residual particles (976 5-min PM_{1.0} samples in total). Sulfate and ammonium dominated the water-soluble mass ($\text{NH}_4^+ + \text{SO}_4^{2-} = 84 \pm 14\%$), while organic acids contributed $3.4 \pm 3.7\%$. The average $\text{NH}_4^+:\text{SO}_4^{2-}$ molar ratio was 1.77 ± 0.85 . Particulate concentrations of organic acids increased with decreasing carbon number from C-9 to C-2. Organic acids were most abundant above cloud, presumably as a result of aqueous phase chemistry in cloud droplets, followed by subsequent droplet evaporation above cloud tops; the main product of this chemistry was oxalic acid. The evolution of organic acids with increasing altitude in cloud provides evidence for the multistep nature of oxalic acid production; predictions from a cloud parcel model are consistent with the observed oxalate: glyoxylate ratio as a function of altitude in GoMACCS cumuli. Suppressed organic acid formation was observed in clouds with relatively acidic droplets, as determined by high particulate nitrate concentrations (presumably high HNO_3 levels too) and lower liquid water content, as compared to other cloud fields

probed. In the Houston Ship Channel region, an area with significant volatile organic compound emissions, oxalate, acetate, formate, benzoate, and pyruvate, in decreasing order, were the most abundant organic acids. Photo-oxidation of m-xylene in laboratory chamber experiments leads to a particulate organic acid product distribution consistent with the Ship Channel area observations.

Starry, O. S., H. M. Valett, et al. (2005). "Nitrification rates in a headwater stream: influences of seasonal variation in C and N supply." Journal of the North American Benthological Society **24**(4): 753-768.

Nitrification, the chemoautotrophic process by which $\text{NH}_4\text{-N}$ is converted to $\text{NO}_3\text{-N}$, is an integral biogeochemical transformation in stream ecosystems. Previous research has shown that experimental addition of dissolved organic C inhibits rates of nitrification, and that $\text{NH}_4\text{-N}$ addition stimulates rates of nitrification. In many streams, large amounts of C and N may be present in particulate and sorbed forms. Hugh White Creek, a headwater stream located in the southern Appalachian mountains of North Carolina, USA, has very low concentrations of dissolved N and receives large inputs of allochthonous particulate organic matter (POM) each autumn. We conducted a seasonal survey of organic matter (OM) standing stocks and nitrification rates, and we experimentally manipulated dissolved C and N supplies in stream-sediment microcosms to determine: 1) how rates of nitrification compare across seasons, and 2) to what extent nitrification rates are influenced by seasonal changes in standing stocks and relative abundances of particulate, sorbed, and dissolved forms of C and N. Rates of nitrification were closely and positively related to rates of ammonification which, in turn, were negatively related to ON ratios of fine benthic organic matter (FBOM). Uniform additions of dissolved C and N had varying effects on sediment N-transformation rates during different seasons. Variable responses to experimental additions probably reflected the changing relative importance of C and N as sediment OM stocks were depleted and underwent changes in quality. Slow rates of nitrification for much of the year may be attributed to colder temperatures and large quantities of particulate C relative to N. To the extent that changes in POM stocks dictate changes in C and N availability, seasonal OM dynamics are closely linked to rates of nitrification.

Strauss, E. A., W. B. Richardson, et al. (2004). "Nitrification in the Upper Mississippi River: patterns, controls, and contribution to the $\text{NO}_3\text{-}$ budget." Journal of the North American Benthological Society **23**(1): 1-14.

We measured nitrification rates in sediment samples collected from a variety of aquatic habitats in Navigation Pool 8 of the Upper Mississippi River (UMR) 7 times between May 2000 and October 2001. We also conducted nutrient-enrichment experiments and analyzed vertical profiles of sediment to determine factors regulating nitrification. Nitrification rates were relatively high compared to other ecosystems (ranging from 0-8.25 $\mu\text{g N cm}^{-2} \text{ h}^{-1}$) and exhibited significant temporal and spatial patterns. Nitrification rates were greatest during the summer and spring compared to autumn and winter (ANOVA, $p < 0.05$) and were greater in contiguous backwater and impounded habitats

compared to main and side-channel habitats ($p < 0.05$). Regression analysis indicated that nitrification rates were weakly ($r^2 = 0.18$, $p < 0.0001$) related to temperature and exchangeable NH_4^+ of the sediment. However, nutrient-enrichment experiments showed that NH_4^+ availability did not limit nitrification in 3 sediment types with variable organic matter. Vertical profiles of sediment cores demonstrated that oxygen concentration and nitrification had similar patterns suggesting that nitrification may be limited by oxygen penetration into sediments. We conclude that temperature and sediment NH_4^+ can be useful for predicting broad-scale temporal and spatial nitrification patterns, respectively, but oxygen penetration into the sediments likely regulates nitrification rates in much of the UMR. Overall, we estimated that nitrification produces 6982 mt N/y of NO_3^- or 7% of the total annual NO_3^- budget.

Strom, M. E., C. R. Fisher, et al. (1997). "Methanotrophic symbiont location and fate of carbon incorporated from methane in a hydrocarbon seep mussel." Marine Biology **129**(3): 465-476.

Seep Mytilid Ia (SMIa), an undescribed mussel found at hydrocarbon seeps in the Gulf of Mexico, harbors intracellular methanotrophic symbionts. Two techniques were used to address the hypothesis that host digestion of symbionts is a significant mechanism of carbon transfer from symbiont to host in the SMIa association: lysosomal enzyme cytochemistry and C-14 tissue autoradiography. Acid phosphatase activity was consistently localized in the Golgi apparatus and associated vesicles of gill cells, but was detected around bacteria in only three of approximately 50 bacteriocytes examined. These results indicate that the cellular equipment necessary for lysosomal digestion of symbionts is present in host bacteriocytes, but that acid phosphatase activity in symbiont vacuoles is rare at a given point in time. Tissue autoradiography was conducted with mussels collected in September 1992 to document carbon fixation by symbionts and follow the time course of transfer to host tissues. No asymbiotic host cell type showed a significant increase in relative grain density until at least 1 d after the end of incubation with C-14-methane. The ratio of label in the basal portion of bacteriocytes to total bacteriocyte label did not show a significant increase until 10 d after the end of the incubation period, indicating a slow increase of labeled carbon in the putative residual bodies, containing the remnants of lysosomal digestion. These results are consistent with the hypothesis that host digestion of symbionts is one route of nutrient acquisition in SMIa. Intracellular methanotrophic bacteria were found outside of the gill in SMIa juveniles, in mantle and foot epithelial tissues previously believed to be symbiont-free. These extra-gill symbionts and their host cells are morphologically similar to their gill counterparts and, like the gill symbionts, actively fix carbon from methane.

Strom, S. L. and M. W. Strom (1996). "Microplankton growth, grazing, and community structure in the northern Gulf of Mexico." Marine Ecology-Progress Series **130**(1-3): 229-240.

Seawater dilution experiments were conducted during spring and fall in the continental shelf region of the northern Gulf of Mexico. Nutrient-enhanced

phytoplankton growth rates of 0.7 to 2.2 d⁻¹) were measured for the entire phytoplankton community; highest growth rates were associated with >8 μm cells. Phytoplankton growth was nutrient limited in all May experiments, and >8 μm phytoplankton, primarily diatoms, showed the strongest response to nutrient addition: their growth rates increased the most and reached the highest values. Rates of microzooplankton grazing on the entire phytoplankton community were moderate (0 to 0.7 d⁻¹). During a given experiment, patterns of grazing on 2 phytoplankton size fractions (<8 and >8 μm) generally differed, and high rates of grazing (>1 d⁻¹) on both <8 and >8 μm cells were sometimes observed. Across all experiments, grazing by microzooplankton averaged 30% of nutrient-enhanced phytoplankton growth. In May, when phytoplankton growth was strongly nutrient limited, grazing averaged 90% of natural (non-nutrient-enhanced) phytoplankton growth. These data indicate that microzooplankton can be a significant source of phytoplankton mortality, even in eutrophic coastal waters. The microzooplankton community, excluding cells <5 μm, comprised primarily heterotrophic dinoflagellates and aloricate ciliates. These organisms exhibited high net growth rates (mean = 0.8 d⁻¹) during experiments at higher irradiance levels. Ingestion of chain diatoms by the dinoflagellate *Gyrodinium* sp. was observed in preserved samples; such grazing pathways, in which relatively large phytoplankton cells are consumed by protozoa, may be quantitatively important in this coastal ecosystem. Due to the variety of taxa and feeding mechanisms within the microzooplankton, their grazing impact was not restricted to the smallest phytoplankton cells, indicating that size-based models of trophic structure could yield misleading predictions about patterns of energy flow in this coastal ecosystem.

Stutes, J., J. Cebrian, et al. (2007). "Benthic metabolism across a gradient of anthropogenic impact in three shallow coastal lagoons in NW Florida." Marine Ecology-Progress Series **348**: 55-70.

Seagrasses are being lost at alarming rates worldwide, most often due to anthropogenic effects, but few reports have examined how seagrass loss affects the metabolism of coastal ecosystems. Here, we address this question by comparing both areal and system-integrated daytime benthic metabolic rates across 3 lagoons in the North Central Gulf of Mexico that display varying levels of abundance of the shoalgrass *Halodule wrightii* (i.e. from 64 % of the bottom covered with shoalgrass down to between 4 and 0 %), partially due to contrasting anthropogenic pressures. When comparing the 2 shoalgrass-containing lagoons, shoalgrass patches featured higher areal rates of gross primary production (GPP) and respiration (R), and, to a lesser extent, higher rates of net production (NP), than did bare sediment. These results were robust despite across-lagoon differences in percentage cover and areal biomass of shoalgrass and benthic microalgae (i.e. the lagoon with less cover also had lower areal shoalgrass biomass in the shoalgrass patches and higher areal microalgal chlorophyll a concentrations in the sediment). We did not find any consistent differences in the metabolic rates of bare sediment across the 3 lagoons, despite the fact that areal microalgal chlorophyll a concentrations in bare sediment increased as shoalgrass

abundance decreased across the 3 lagoons. System-integrated rates of benthic GPP and R were higher in the lagoon with the highest shoalgrass cover when compared with the lagoons with little or no shoalgrass; but, surprisingly, system-integrated rates of benthic NP did not differ significantly across lagoons. This result suggests that the large decrease in shoalgrass abundance across the lagoons examined does not greatly affect the lagoon's potential capacity for accumulation and/or export of organic carbon. It also underlines the importance of deriving system-integrated estimates to properly understand how decreasing seagrass abundance can alter the daytime metabolism of coastal systems.

Surge, D. M. and K. C. Lohmann (2002). "Temporal and spatial differences in salinity and water chemistry in SW Florida estuaries: Effects of human-impacted watersheds." Estuaries **25**(3): 393-408.

Three estuaries near Naples, Florida with variably modified watersheds have been investigated to understand the chemical consequences of altering drainage patterns. Blackwater River (near natural drainage, control site), Henderson Creek (moderately modified watershed), and Faka-Union Canal (severe channelization) were sampled for temperature, salinity, $\delta(18)\text{O}$, $\delta(13)\text{C}$ of dissolved inorganic carbon (DIC), molality of CO_2 (ΣCO_2), and Mg:Ca and Sr:Ca ratios between freshwater and marine water end members over a 17-mo period. Carbon isotope composition followed similar seasonal patterns as salinity. Freshwater and seawater end members are more negative than the global average, likely reflecting equilibration with local carbon sources derived from mangrove leaf litter and groundwater. $\delta(13)\text{C}$ responds to differences in primary productivity between estuaries. Henderson Creek has higher primary productivity than Blackwater River (probable due to higher sewage input and agricultural runoff) and has more positive $\delta(13)\text{C}$ and lower ΣCO_2 . $\delta(18)\text{O}$ is affected by seasonal input of freshwater from atmospheric precipitation, evaporation, and groundwater. Late summer and fall rains lower the $\delta(18)\text{O}$ of estuarine water, whereas evaporative conditions in the dry season elevate $\delta(18)\text{O}$ to values that can be more positive upstream than those from the Gulf of Mexico (estuarine inversion). Evaporation produces water in the Gulf of Mexico that is > 1 parts per thousand more positive than the global sea surface average most of the year. The very negative $\delta(18)\text{O}$ values in Blackwater River and Henderson Creek likely reflect atmospheric and groundwater contribution. Mg:Ca and Sr:Ca ratios of Gulf water from all three estuaries are similar to global averages at low latitudes. Freshwater end members among estuaries are different in that Blackwater River has higher ratios, suggesting a groundwater contribution. Dolomitic rocks in the subsurface likely provide a source of Mg ions.

Sutula, M., T. S. Bianchi, et al. (2004). "Effect of seasonal sediment storage in the lower Mississippi River on the flux of reactive particulate phosphorus to the Gulf of Mexico." Limnology and Oceanography **49**(6): 2223-2235.

The annual surface water flux of total reactive (i.e., potentially bioavailable) particulate P from the Mississippi River was estimated by measuring the reactive

(including labile, iron, organic, and calcium bound) and nonreactive (detrital) P phases in suspended particulates in the Mississippi River. In addition, the transformation of the major sediment P phases resulting from seasonal channel storage and resuspension was examined. Samples were collected during five cruises over 1 yr at marine and riverine sites. Solid-phase and pore-water nutrients were quantified, and solid-phase P pools were measured using a sequential extraction technique. These results indicate that the Mississippi River exports 134×10^6 kg yr⁻¹ of total reactive P via surface water. Seasonal hydrological forcing controlled the variability in major P phases found in channel sediments through hydrodynamic sorting. Although the 6-9-month time period during which sediments were stored in the river channel was sufficient to see evidence of early diagenesis in the pore waters, no significant net effect was seen on major P phase distribution. The loss of a significant percentage of labile and iron-bound P appears to be occurring only as these riverine sediments are deposited and reworked on the continental shelf.

Sutula, M. A., B. C. Perez, et al. (2003). "Factors affecting spatial and temporal variability in material exchange between the Southern Everglades wetlands and Florida Bay (USA)." Estuarine Coastal and Shelf Science **57**(5-6): 757-781.

Physical and biological processes controlling spatial and temporal variations in material concentration and exchange between the Southern Everglades wetlands and Florida Bay were studied for 2.5 years in three of the five major creek systems draining the watershed. Daily total nitrogen (TN), and total phosphorus (TP) fluxes were measured for 2 years in Taylor River, and ten 10-day intensive studies were conducted in this creek to estimate the seasonal flux of dissolved inorganic nitrogen (N), phosphorus (P), total organic carbon (TOC), and suspended matter. Four 10-day studies were conducted simultaneously in Taylor, McCormick, and Trout Creeks to study the spatial variation in concentration and flux. The annual fluxes of TOC, TN, and TP from the Southern Everglades were estimated from regression equations. The Southern Everglades watershed, a 460-km² area that includes Taylor Slough and the area south of the C-111 canal, exported 7.1 g C m⁻², 0.46 g N m⁻², 0.007 g P m⁻², annually. Everglades P flux is three to four orders of magnitude lower than published flux estimates from wetlands influenced by terrigenous sedimentary inputs. These low P flux values reflect both the inherently low P content of Everglades surface water and the efficiency of Everglades carbonate sediments and biota in conserving and recycling this limiting nutrient. The seasonal variation of freshwater input to the watershed was responsible for major temporal variations in N, P, and C export to Florida Bay; approximately 99% of the export occurred during the rainy season. Wind-driven forcing was most important during the later stages of the dry season when low freshwater head coincided with southerly winds, resulting in a net import of water and materials into the wetlands. We also observed an east to west decrease in TN: TP ratio from 212: 1 to 127: 1. Major spatial gradients in N: P ratios and nutrient concentration and flux among the creek were consistent with the westward decrease in surface water runoff from the P-limited Everglades and increased advection of relatively

P-rich Gulf of Mexico (GOM) waters into Florida Bay. Comparison of measured nutrient flux from Everglades surface water inputs from this study with published estimates of other sources of nutrients to Florida Bay (i.e. atmospheric deposition.. anthropogenic inputs from the Florida Keys, advection from the GOM) show that Everglades runoff represents only 2% of N inputs and 0.5% of P input to Florida Bay. (C) 2003 Elsevier Ltd. All rights reserved.

Swart, P. K., G. F. Healy, et al. (1996). "The stable oxygen and carbon isotopic record from a coral growing in Florida Bay: A 160 year record of climatic and anthropogenic influence." Palaeogeography Palaeoclimatology Palaeoecology **123**(1-4): 219-237.

A 160 year record of skeletal $\delta(13)\text{C}$ and $\delta(18)\text{O}$ was examined in a specimen of the coral *Solenastrea bournoni* growing in Florida Bay. Variations in the $\delta(18)\text{O}$ of the skeleton can be correlated to changes in salinity while changes in the $\delta(13)\text{C}$ reflect cycling of organic material within the Bay. Based on the correlation between salinity and skeletal $\delta(18)\text{O}$, we have concluded that there has been no long term increase in salinity in this area of Florida Bay over the past 160 years. Using salinity correlations between the various basins obtained from instrumental data, we have been able to extend our interpretations to other parts of Florida Bay reaching similar conclusions. In contrast to current ideas which have focused on changes in Florida Bay water quality over the past 20-yr history of the Bay as causative in its decline, we have determined that changes in water quality in this basin were already set in motion between 1905 and 1912 by the construction of the Florida East Coast Railway from Miami to Key West. The construction of the railway resulted in the restriction of the exchange of water between the Florida reef tract and the Gulf of Mexico causing Florida Bay to become more eutrophic. Evidence of this process is observed in the sudden shift to relatively lower $\delta(13)\text{C}$ values coincident with railway construction. Natural events also appear to have influenced the water in the Bay. Between 1912 and 1948 frequent hurricanes had the effect of increasing exchange of water between the Bay and reef tract and removing large quantities of organic rich sediments. However, since 1948 the number of hurricanes affecting the area has decreased and the products of the oxidation of organic material have been increasingly retained within the basin promoting the initiation of eutrophic conditions.

Swarzenski, P. W., P. L. Campbell, et al. (2008). "A 1000-year sediment record of recurring hypoxia off the Mississippi River: The potential role of terrestrially-derived organic matter inputs." Marine Chemistry **109**(1-2): 130-142.

A suite of inorganic and organic geochemical tracers and a low-oxygen tolerant benthic faunal index ('PEB') were measured in a C-14-dated 2+ m long gravity core collected on the Louisiana shelf adjacent to the Mississippi River delta to study potential millennium-scale low-oxygen events. Periodic down-core excursions in the PEB index throughout the core suggest recurring, natural bottom water low-oxygen events that extend back similar to 1000 C-14 years. Select trace element and biomarker distributions in these same sediments were examined as potential tracers of past hypoxic events and to help distinguish

between marine versus terrestrial processes involved in organic carbon production. In discrete sediment horizons where the PEB index was elevated, redox-sensitive vanadium concentrations were consistently depleted, excursions in sedimentary $\delta C-13$ suggest periodic, preferential terrestrial inputs, and the concentrations of two sterol biomarkers (sitosterol and beta-stigmasterol) also showed concurrent enrichments. If the PEB index successfully records similar to 1000 C-14 year-scale low-oxygen events, then the distribution of these geochemical tracers can be interpreted to corroborate the view that naturally occurring low-oxygen bottom water conditions have existed on the inner Louisiana continental shelf, not only in recent times, but also over at least the last 1000 C-14 years. These data support the general hypothesis that historic, low-oxygen bottom water conditions on the Louisiana shelf are likely tied to periods of increased fluvial discharge and associated wetland export in the absence of modern river levees. Enhanced river discharge and associated material export would both stimulate enhanced in situ organic carbon production and foster water column stratification. Such periodic elevated river flows during the last millennium can be linked to climate fluctuations and tropical storm activity. (c) 2008 Elsevier B.V. All rights reserved.

Tester, P. A. and J. T. Turner (1988). "COMPARATIVE CARBON-SPECIFIC INGESTION RATES OF PHYTOPLANKTON BY ACARTIA-TONSA, CENTROPAGES-VELIFICATUS AND EUCALANUS-PILEATUS GRAZING ON NATURAL PHYTOPLANKTON ASSEMBLAGES IN THE PLUME OF THE MISSISSIPPI RIVER (NORTHERN GULF OF MEXICO CONTINENTAL-SHELF)." Hydrobiologia **167**: 211-217.

Thayer, G. W., J. J. Govoni, et al. (1983). "STABLE CARBON ISOTOPE RATIOS OF THE PLANKTONIC FOOD WEB IN THE NORTHERN GULF OF MEXICO." Bulletin of Marine Science **33**(2): 247-256.

Tiquia, S. M., S. A. Masson, et al. (2006). "Vertical distribution of nitrite reductase genes (*nirS*) in continental margin sediments of the Gulf of Mexico." Fems Microbiology Ecology **58**(3): 464-475.

Marine sediments account for up to 66% of the loss of nitrogen load to coastal areas. Sedimentary denitrification is the main sink for fixed nitrogen in the global nitrogen budget, and thus it is important to understand the structure and composition of denitrifying communities. To understand the structure and composition of denitrifying communities, the diversity of nitrite reductase (*nirS*) genes from sediments along the Gulf of Mexico was examined using a PCR-based cloning approach. Sediments were collected at three different depths (0-0.5, 4-5 and 19-21 cm). Geochemical analysis revealed decreasing nitrate and oxygen concentrations with increasing sediment depth. This trend coincided with the decrease in diversity of denitrifying bacteria. LIBSHUFF analysis indicated that the clone library in the shallowest sediment (depth, 0-0.5 cm) was significantly different from that in the deepest sediment (depth, 19-21 cm), and that the deeper sediments (depths of 4-5 and 19-21 cm) were significantly

similar. Community structural shifts were evident between the shallowest (oxic zone) and deepest (anoxic zone) sediments. Community changes within the deepest sediments were more subtle, with the presence of different nirS clone sequences gradually becoming dominant or, alternatively, decreasing with depth. The changes in community structure at this depth are possibly driven by nutrient availability, with lower quality sources of carbon and energy leading to the disappearance of nirS sequences common in the top layer. The majority of recovered nirS sequences were phylogenetically divergent relative to known denitrifying bacteria in the database.

Torbert, H. A. and K. N. Potter (2004). Fertility management effects on runoff losses of phosphorus. Environmental Impact of Fertilizer on Soil and Water. **872**: 220-234.

Most agricultural soils are deficient in at least one of the essential nutrients for plant growth, or the complex processes of nutrient cycling interact to limit their availability. These nutrients are commonly added to soil as fertilizers in either inorganic or organic forms. However, poor application of fertilizers (both inorganic and organic) can lead to nutrient loss from agricultural land by runoff and leaching. These potential non-point source nutrient losses can contribute to environmental degradation, eutrophication of surface waters, and possible human health risks. These concerns have been stimulated by blooms of the toxic dinoflagellate algae (*Pfiesteria piscicidia*) that have caused fish kills and human illnesses and by reports of a hypoxic area (low dissolved oxygen) in the Gulf of Mexico (20,000 km²) (1), which have been attributed to pollution from excess nutrients (2). Nonpoint source pollution from agriculture has been identified as the leading source of water quality reduction by the USEPA (3), with estimates that agriculture affects the degradation of 60% of river miles, 50% of lake acres, and 34% of estuaries acres. While these impairments are not nutrient specific, both N and P have been implicated in causing accelerated eutrophication. The role of nutrients in the eutrophication process is very complex, but in general, lake eutrophication is associated with P, N is associated with ocean waters, and both N and P are associated with estuaries (4, 5). Factors affecting non-point loss of nutrients from agricultural soils are numerous and complex. Many of the factors that affect nutrient losses can be greatly impacted by agricultural management practices. Scientists have continued to research and develop methods to improve agricultural practices to reduce nutrient losses.

Tornqvist, T. E., J. L. Gonzalez, et al. (2004). "Deciphering Holocene sea-level history on the US Gulf Coast: A high-resolution record from the Mississippi Delta." Geological Society of America Bulletin **116**(7-8): 1026-1039.

Published Holocene relative sea-level (RSL) curves for the U.S. Gulf Coast are in mutual conflict, with some characterized by a smooth RSL rise akin to widely accepted eustatic sea-level curves versus others, including several recent ones, that are characterized by a conspicuous "stair-step" pattern with prolonged (millennium-scale) RSL stillstands alternating with rapid (meter-scale) rises. In addition, recent work in Texas and Alabama has revitalized the notion of a middle Holocene RSL highstand, estimated at 2 m above present mean sea level. An

extensive sampling program in the Mississippi Delta (Louisiana) focused on the collection of basal peats that accumulated during the initial transgression of the pre-existing, consolidated Pleistocene basement. We used stable carbon isotope ratios to demonstrate that many of these samples accumulated in environments affected by frequent saltwater intrusion in the <30 cm zone between mean spring high water and mean sea level, and we selected plant macrofossils that were subjected to AMS C-14 dating. Nearly 30 sea-level index points from a similar to 20 km² study area on the eastern margin of the delta suggest that RSL rise followed a relatively smooth trend for the time interval 8000-3000 cal yr B.P., thus questioning the occurrence of major RSL stillstands alternating with abrupt rises. Given the narrow error envelope defined by our data set, any sea-level fluctuations, if present, would have amplitudes of <1 m. Although a true middle Holocene highstand never occurred in the Mississippi Delta, the high level of detail of our time series enables a rigorous test of this hypothesis. Correction of our data set for a hypothetical tectonic subsidence rate of 1.1 mm yr⁻¹ (assuming a constant subsidence rate compared to the tectonically relatively stable adjacent coast of Texas) leads to sea levels near 2 m above present during the time interval 6000-4000 cal yr B.P. However, this model also implies a RSL position near -2 m around 8000 cal yr B.P, which is inconsistent both with data of this age from Texas, as well as with widely accepted sea-level data from elsewhere. We therefore conclude that a middle Holocene highstand for the U.S. Gulf Coast is highly unlikely, and that the entire area is still responding glacio-isostatically, by means of forebulge collapse, to the melting of the Laurentide Ice Sheet.

Trefry, J. H., S. Metz, et al. (1994). "TRANSPORT OF PARTICULATE ORGANIC-CARBON BY THE MISSISSIPPI RIVER AND ITS FATE IN THE GULF-OF-MEXICO." *Estuaries* **17**(4): 839-849.

This study was designed to determine the amount of particulate organic carbon (POC) introduced to the Gulf of Mexico by the Mississippi River and assess the influence of POC inputs on the development of hypoxia and burial of organic carbon on the Louisiana continental shelf. Samples of suspended sediment and supporting hydrographic data were collected from the river and >50 sites on the adjacent shelf. Suspended particles collected in the river averaged 1.8 +/- 0.3% organic carbon. Because of this uniformity, POC values (in $\mu\text{mol l}^{-1}$) correlated well with concentrations of total suspended matter. Net transport of total organic carbon by the Mississippi-Atchafalaya River system averaged 0.48×10^{12} moles y^{-1} with 66% of the total organic carbon carried as POC. Concentrations of POC decreased from as high as 600 $\mu\text{mol l}^{-1}$ in the river to <0.8 $\mu\text{mol l}^{-1}$ in offshore waters. In contrast, the organic carbon fraction of the suspended matter increased from <2% of the total mass in the river to >35% along the shelf at greater than or equal to 10 km from the river mouth. River flow was a dominant factor in controlling particle and POC distributions; however, time-series data showed that tides and weather fronts can influence particle movement and POC concentrations. Values for apparent oxygen utilization (AOU) increased from similar to 60 $\mu\text{mol l}^{-1}$ to >200 $\mu\text{mol l}^{-1}$ along the

shelf on approach to the region of chronic hypoxia. Short-term increases in AOU were related to transport of more particle-rich waters. Sediments buried on the shelf contained less organic carbon than incoming river particles. Organic carbon and $\delta^{13}\text{C}$ values for shelf sediments indicated that large amounts of both terrigenous and marine organic carbon are being decomposed in shelf waters and sediments to fuel observed hypoxia.

Triska, F. J., J. H. Duff, et al. (2007). "DIN retention-transport through four hydrologically connected zones in a headwater catchment of the Upper Mississippi River." Journal of the American Water Resources Association **43**(1): 60-71.

Dissolved inorganic nitrogen (DIN) retention-transport through a headwater catchment was synthesized from studies encompassing four distinct hydrologic zones of the Shingobee River Headwaters near the origin of the Mississippi River. The hydrologic zones included: (1) hillslope ground water (ridge to bankside riparian); (2) alluvial riparian ground water; (3) ground water discharged through subchannel sediments (hyporheic zone); and (4) channel surface water. During subsurface hillslope transport through Zone 1, DIN, primarily nitrate, decreased from similar to 3 mg-N/l to < 0.1 mg-N/l. Ambient seasonal nitrate:chloride ratios in hillslope flow paths indicated both dilution and biotic processing caused nitrate loss. Biologically available organic carbon controlled biotic nitrate retention during hillslope transport. In the alluvial riparian zone (Zone 2) biologically available organic carbon controlled nitrate depletion although processing of both ambient and amended nitrate was faster during the summer than winter. In the hyporheic zone (Zone 3) and stream surface water (Zone 4) DIN retention was primarily controlled by temperature. Perfusion core studies using hyporheic sediment indicated sufficient organic carbon in bed sediments to retain ground water DIN via coupled nitrification-denitrification. Numerical simulations of seasonal hyporheic sediment nitrification-denitrification rates from perfusion cores adequately predicted surface water ammonium but not nitrate when compared to 5 years of monthly field data (1989-93). Mass balance studies in stream surface water indicated proportionally higher summer than winter N retention. Watershed DIN retention was effective during summer under the current land use of intermittently grazed pasture. However, more intensive land use such as row crop agriculture would decrease nitrate retention efficiency and increase loads to surface water. Understanding DIN retention capacity throughout the system, including special channel features such as sloughs, wetlands and floodplains that provide surface water-ground water connectivity, will be required to develop effective nitrate management strategies.

Turner, R. E., C. S. Milan, et al. (2004). "A retrospective analysis of trace metals, C, N and diatom remnants in sediments from the Mississippi River delta shelf." Marine Pollution Bulletin **49**(7-8): 548-556.

The development of oil and gas recovery offshore of the Mississippi River delta began in shallow water in the 1950s, expanded into deeper waters, and peaked in the 1990s. This area of the outer continental shelf (OCS) is the historical and present location of >90% of all US OCS oil and gas production and reserves. The

juxtaposition of its 4000 producing platforms, recovering \$10 billion yr⁻¹) of oil, gas and produced water in the same area where about 28% of the US fisheries catch (by weight) is made and near 40% of the US coastal wetlands, makes this an area worth monitoring for regional pollutant loading. This loading may come from several sources, including sources related to OCS development, but also from the Mississippi River watershed. In this context, any contaminant loading on this shelf may be neither detectable nor significant against a background of climatic or biological variability. We examined the sedimentary record for indicators of industrial by products from OCS oil and gas development and of industrial products entering via the Mississippi River, primarily using vanadium (V) and barium (Ba) concentrations normalized for aluminum (M). Barium is primarily used in drilling muds in the form of barite, whereas V is an important strengthening component of metal alloys, including steel. The fluctuations in the accumulation of Ba, but not V, were coincidental with the presumed use of barite. The fluctuations in V concentration in the sediments were coincidental with the national consumption of V. Copper (Cu), cadmium (Cd) and zinc (Zn) concentrations in sediments fluctuate coincidentally with V, not Ba, thus indicating that the dominant source of these trace metals in offshore sediments were derived from riverine sources, and were not primarily from in situ industrial processes releasing them on the shelf. This is not to suggest that local site-specific contamination is not a significant management or health concern. The low oxygen (hypoxia; less than or equal to 2 mg l⁻¹) zone that consistently covers much of this continental shelf's bottom layer in summer is attributed to nitrate loading from the Mississippi River. Increased nitrogen loading from river to shelf stimulates diatom production whose loading to the bottom layer and subsequent metabolism results in oxygen being depleted faster than it is replaced. In the last two decades there has been an increased accumulation of organic matter in sediments near the mouth of the Mississippi River. This coupling between river water, surface water and bottom water has recently expanded westward of the Atchafalaya River delta towards the Texas coast. The accumulation of biogenic silica (BSi) and carbon in dated sediments is coincidental with variations in riverine nitrate flux, but not with either V or Ba accumulation rates. These analyses indicate that both OCS development and riverine sources exert strong influences on the sediment constituents offshore, and that these influences may be independent of one another. (C) 2004 Elsevier Ltd. All rights reserved.

Turner, R. E. and N. N. Rabalais (2004). "Suspended sediment, C, N, P, and Si yields from the Mississippi River Basin." *Hydrobiologia* **511**(1): 79-89.

The annual loads of C, N, P, silicate, total suspended sediment (mass) and their yields (mass area⁻¹) were estimated for six watersheds of the Mississippi River Basin (MRB) using water quality and water discharge records for 1973 to 1994. The highest load of suspended sediments is from the Missouri watershed (58 mt km² yr⁻¹), which is also the largest among the six major sub-basins. The Ohio watershed delivers the largest load of water (38%). The Upper Mississippi has the largest total nitrogen load (32%) and yield (1120 kg TN km² yr⁻¹). The

loading of organic carbon, total phosphorus and silicate from the Upper Mississippi and Ohio watersheds are similar and relatively high (range 2.1 - 2.5, 0.068 - 0.076, and 0.8 - 1.1 mt km² yr⁻¹), respectively). The yields of suspended sediments, total phosphorus, total nitrogen, and silicate from the Lower Mississippi watershed are disproportionately the highest for its area, which is the smallest of all the watersheds and has the weakest monitoring network. The loading from the Red and Arkansas watersheds are of lesser importance than the others for most parameters investigated. The total nitrogen loading to coastal waters increased an additional 150% since the early 1900s, and is now dominated by loads from the Upper Mississippi watershed, rather than the previously dominant Ohio watershed. An analysis of trends for 1973 - 1994 suggests variability among years, rather than uni-directional change for most variables among 11 key stations. Explanatory relationships were established or confirmed to describe TN and TP loadings in terms of the now largely human-created landscape arising mostly over the last 150 years.

Turner, R. E., N. N. Rabalais, et al. (2007). "Characterization of nutrient, organic carbon, and sediment loads and concentrations from the Mississippi River into the Northern Gulf of Mexico." Estuaries and Coasts **30**(5): 773-790.

We synthesize and update the science supporting the Action Plan for Reducing, Mitigating, and Controlling Hypoxia in the Northern Gulf of Mexico (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force 2001) with a focus on the spatial and temporal discharge and patterns of nutrient and organic carbon delivery to the northern Gulf of Mexico, including data through 2006. The discharge of the Mississippi River watershed over 200 years varies but is not demonstrably increasing or decreasing. About 30% of the Mississippi River was shunted westward to form the Atchafalaya River, which redistributed water and nutrient loads on the shelf. Data on nitrogen concentrations from the early 1900s demonstrate that the seasonal and annual concentrations in the lower river have increased considerably since then, including a higher spring loading, following the increase in fertilizer applications after World War II. The loading of total nitrogen (TN) fell from 1990 to 2006, but the loading of total phosphorus (TP) has risen slightly, resulting in a decline in the TN:TP ratios. The present TN:TP ratios hover around an average indicative of potential nitrogen limitation on phytoplankton growth, or balanced growth limitation, but not phosphorus limitation. The dissolved nitrogen:dissolved silicate ratios are near the Redfield ratio indicative of growth limitations on diatoms. Although nutrient concentrations are relatively high compared to those in many other large rivers, the water quality in the Mississippi River is not unique in that nutrient loads can be described by a variety of land-use models. There is no net removal of nitrogen from water flowing through the Atchafalaya basin, but the concentrations of TP and suspended sediments are lower at the exit point (Morgan City, Louisiana) than in the water entering the Atchafalaya basin. The removal of nutrients entering offshore waters through diversion of river water into wetlands is presently less than 1% of the total loadings going directly offshore, and would be less than 8% if the 10,093 km² of coastal wetlands were successfully engineered for that

purpose. Wedand loss is an insignificant contribution to the carbon loading offshore, compared to in situ marine production. The science-based conclusions in the Action Plan about nutrient loads and sources to the hypoxic zone off Louisiana are sustained by research and monitoring occurring in the subsequent 10 years.

Turner, R. E., N. N. Rabalais, et al. (2006). "Paleo-indicators and water quality change in the Charlotte Harbor estuary (Florida)." Limnology and Oceanography **51**(1): 518-533.

We reconstructed water quality changes for 1800 to 2000 in Charlotte Harbor (Florida), a shallow subtropical estuary, by using a suite of biological and geochemical proxies in dated sediments collected in the region of a present day, midsummer hypoxic zone. The declining freshwater loading into the estuary from 1931 to the 1980s is not the probable causal agent encouraging the appearance or expansion of a hypoxia zone (measuring up to 90 km² in summer). Rather, the reconstructed trends in nitrogen loading indicate increased phytoplankton production has likely caused a decline in bottom water oxygen concentrations. Sedimentary biogenic silica (BSi), carbon, nitrogen, and phosphorus concentrations increased concurrently with known or inferred changes in nutrient loadings. There were direct relationships between phytoplankton pigments and BSi, heavier delta S-14 with increased carbon loading, and sequestration of P, Al, and Fe as carbon loading increased. The results from the sediment analyses and the results from mixing models using C : N ratios and delta C-13 suggest an estuarine system that is responsive to increased carbon loading from the nitrogen-limited phytoplankton community and whose sediments are becoming increasingly anoxic as a result. The present nitrogen loading is about three times above that prior to the 1800s, suggesting that without management intervention the anticipated doubling of the watershed's population from 1990 to 2020 will greatly increase the nitrogen loading to this estuary and will lead to much higher amounts of phytoplankton biomass and accumulation and exacerbate hypoxic conditions.

Turner, R. E., N. N. Rabalais, et al. (2006). "Predicting summer hypoxia in the northern Gulf of Mexico: Riverine N, P, and Si loading." Marine Pollution Bulletin **52**(2): 139-148.

We conducted a statistical analysis to discern the relative strengths of the loading of various forms of nitrogen, phosphorus, dissolved silicate and their molar ratios on the variance in the size of the summertime low oxygen zone found off the Mississippi River, northern Gulf of Mexico. A stable statistical model that included Year and riverine nitrate + nitrite loading for the 2 months prior to the measurement of hypoxic zone size described 82% of its variation in size from 1978 to 2004. The usefulness of the term Year is consistent with the documented increase in carbon stored in sediments after the 1970s, which is when the hypoxic zone is predicted to have become a regular feature on the shelf and to have expanded westward. The increased carbon storage is anticipated to cause a sedimentary respiratory demand influencing the size of the zone, and whose temporal influence is cumulative and transcends the annual variations in nitrogen

loading. The variable Year is negatively correlated with the TN:TP ratio in a way that suggests N, not P, has become more important as a factor limiting phytoplankton growth in the last 20 years. Nitrogen, in particular nitrate + nitrite, and not phosphorus, dissolved silicate, or their molar ratios, appears to be the major driving factor influencing the size of the hypoxic zone on this shelf. This conclusion is consistent with cross-system analyses that conclude that the TN:TP ratio in the Mississippi River, currently fluctuating around 20:1, is indicative of nitrogen, not phosphorus, limitation of phytoplankton growth. Nutrient management that places stronger emphasis on reducing nitrogen loading as compared to phosphorus loading, is justified. (c) 2005 Elsevier Ltd. All rights reserved.

Turner, R. E., N. N. Rabalais, et al. (2008). "Gulf of Mexico hypoxia: Alternate states and a legacy." Environmental Science & Technology **42**(7): 2323-2327.

A 20+ year data set of the size of the hypoxic zone off the Louisiana-Texas coast is analyzed to reveal insights about what causes variation in the size of the hypoxic zone in summer, the accumulation of carbon storage in sediments, and pelagic and sediment oxygen demand. The results of models support the conclusion that some of this variation can be explained by a higher sedimentary oxygen demand, which may be larger than water column respiration rates in summer. Proxies for organic loading to sediments reveal that carbon losses continue after accumulation, and results from other studies indicate that sediment oxygen demand is directly related to surface water phytoplankton production, which has increased because of higher nutrient loading from the Mississippi River watershed. The potential size of the hypoxic zone for a given nitrogen load has increased as a result and has doubled from 1980 to 2000. The development of widespread hypoxia after the early 1980s and its consequences could therefore be considered a shift to an alternate ecosystem state. The Action Plan for Reducing, Mitigating and Controlling Hypoxia in the Northern Gulf of Mexico goal of reducing the size of the hypoxic zone to an average of 5000 km² by 2015 becomes more difficult to achieve for every year there is no significant reduction in nutrient loading. The decisions made to reduce the size of the hypoxic zone must incorporate these nonlinear responses and, we think, err on the side of caution in assuming that existing management efforts are sufficient to restore water quality on this shelf. The legacy of a higher sediment respiratory demand following eutrophication should apply to other coastal systems.

Ullah, S. and S. P. Faulkner (2006). "Denitrification potential of different land-use types in an agricultural watershed, lower Mississippi valley." Ecological Engineering **28**(2): 131-140.

Expansion of agricultural land and excessive nitrogen (N) fertilizer use in the Mississippi River watershed has resulted in a three-fold increase in the nitrate load of the river since the early 1950s. One way to reduce this nitrate load is to restore wetlands at suitable locations between croplands and receiving waters to remove run-off nitrate through denitrification. This research investigated denitrification potential (DP) of different land uses and its controlling factors in an

agricultural watershed in the lower Mississippi valley (LMV) to help identify sites with high DP for reducing run-off nitrate. Soil samples collected from seven land-use types of an agricultural watershed during spring, summer, fall and winter were incubated in the laboratory for DP determination. Low-elevation clay soils in wetlands exhibited 6.3 and 2.5 times greater DP compared to high-elevation silt loam and low-elevation clay soils in croplands, respectively DP of vegetated-ditches was 1.3 and 4.2 times that of un-vegetated ditches and cultivated soils, respectively. Soil carbon and nitrogen availability, bulk density, and soil moisture significantly affected DP. These factors were significantly influenced in turn by landscape position and land-use type of the watershed. It is evident from these results that low-elevation, fine-textured soils under natural wetlands are the best locations for mediating nitrate loss from agricultural watersheds in the LMV Landscape position and land-use types can be used as indices for the assessment/modeling of denitrification potential and identification of sites for restoration for nitrate removal in agricultural watersheds. (c) 2006 Elsevier B.V. All rights reserved.

Van Cappellen, P., E. Viollier, et al. (1998). "Biogeochemical cycles of manganese and iron at the oxic-anoxic transition of a stratified marine basin (Orca Basin, Gulf of Mexico)." Environmental Science & Technology **32**(19): 2931-2939.

Chemical distributions and microbial culture data are combined to identify the biogeochemical pathways that control the cycles of manganese and iron at the oxic-anoxic transition of the Orca Basin. The redox transition coincides with an increase in salinity from 35 to 260 parts per thousand; hence, mixing diagrams are used to constrain the salinity ranges over which consumption or production of solute species takes place. Analysis shows that the very high dissolved Mn(II) levels ($>400 \mu\text{M}$) at intermediate salinities (60-180 parts per thousand) result from dissimilatory (microbial) reduction of manganese oxides, coupled to organic matter oxidation. The manganese oxides are continuously regenerated in the oxygenated, low-salinity region (45-52 parts per thousand) by microbial oxidation of dissolved Mn(II). Precipitation of manganese carbonate in the high-salinity zone (>180 parts per thousand) is the main removal mechanism of Mn to the sediments. Upward diffusing Fe(II) ions are extracted from solution within the anoxic, high-salinity range (230-260 parts per thousand), through anaerobic oxidation by manganese oxides or a nonoxidative sorption process. Ferric oxyhydroxides are reduced by reaction with dissolved sulfide and are, therefore, not an important terminal electron acceptor for organic matter oxidation. Overall, the acid-base chemistry, redox transformations, and microbial activity across the salinity transition are strongly coupled to the cycle of manganese.

Vardaro, M. F., I. R. MacDonald, et al. (2006). "Dynamic processes observed at a gas hydrate outcropping on the continental slope of the Gulf of Mexico." Geo-Marine Letters **26**(1): 6-15.

A deep-sea time-lapse camera and several temperature probes were deployed on the Gulf of Mexico continental shelf at a biological community associated with a gas hydrate outcropping to study topographic and hydrologic changes over

time. The deployment site, Bush Hill (GC-185), is located at 27 degrees 47.5' N and 91 degrees 15.0' W at depths of similar to 540 m. The digital camera recorded one still image every 6 h for July-October in 2001, every 2 h for the month of June 2002, and every 6 h for the month of July 2002. Temperature probes were in place at the site for the entire experimental period. The data recovered provide a record of processes that occur at gas hydrate mounds. Sediment resuspension over the mound causes significant variation in luminosity of the time-lapse photographs. A marked diurnal pattern can be seen in the temperature and luminosity records. No major change in shape or size of the gas hydrate outcrop at this site was observed during this study. Stable topography of the gas hydrate mound, combined with high bacterial activity and sediment turnover, appears to focus biological activity in the mound area. Frequency and recurrence of sediment resuspension indicate that short-term change in the depth and distribution of surface sediments is a feature of the benthos at the site. Because the sediment interface is a critical environment for hydrocarbon oxidation and chemosynthesis, short-term variability and heterogeneity may be important characteristics of these settings.

Verdugo, P., A. L. Alldredge, et al. (2004). "The oceanic gel phase: a bridge in the DOM-POM continuum." Marine Chemistry **92**(1-4): 67-85.

Recent discoveries reveal that polymer gel particles are abundant and important in the microbial loop, sedimentation processes, biogeochemical cycling, marine carbohydrate chemistry, and particle dynamics in the ocean. The novelty of these discoveries elicited an interdisciplinary discussion among investigators working in marine geochemistry, microbiology, and polymer physics on the significance of gels in the functioning of marine ecosystems. Marine gels are three-dimensional networks of biopolymers imbedded in seawater. They range in size from single macromolecules entwined, forming single-chain colloidal networks, to assembled polymer networks several hundreds of microns or larger. Gels can form in minutes to hours from dissolved organic matter or polymer chains released by phytoplankton or bacteria. They enclose nanoscale microenvironments that exhibit emerging physical, chemical, and biological properties that are drastically different from those of the DOM polymers that make them. Previous studies show that similar to 10% of surface DOM could be assembled as gels, yielding estimates of similar to 70×10^{15} g of organic carbon. This figure exceeds the global biomass of marine organisms by a factor of 50. The potential huge magnitude of the oceanic gel organic matter (GOM) pool suggests a need to develop reliable quantitative methods to systematically investigate the budget of marine gels and their role in biogeochemical cycling. Gels are particularly important for carbon cycling in that they provide an abiotic mechanism to move organic molecules up the particle size spectrum to sizes capable of sedimentation and eventual sequestration in the deep sea. Macrogels such as transparent exopolymer particles (TEP) are especially significant in sedimentation processes because they appear to be critical for the formation of marine snow and the aggregation of diatom blooms. The discovery of highly abundant gels in seawater also fundamentally changes how we think about the

physical nature and microscale structure of the fluid and organic matter field encountered by bacteria, protists, and viruses in the sea. Gels may serve as nutrients and/or attachment surfaces for microbes, as refuges from predation, and as hot spots of high substrate concentration. Investigation of gels in the ocean represents an important new area of research ripe for exciting discovery. Areas where future research should be focused include the following: (1) determination of the budgets and pool sizes of gels, (2) investigation of the role of gels in biogeochemical cycling, (3) reconciliation of polymer physics and aggregation theory as explanations for macrogel formation, (4) quantification of the role of gels in sedimentation processes and particle dynamics and, (5) assessment of the role of gels as microhabitats, food sources, and attachment surfaces for marine organisms. (C) 2004 Published by Elsevier B.V.

Volkman, J. K. and E. Tanoue (2002). "Chemical and biological studies of particulate organic matter in the ocean." Journal of Oceanography **58**(2): 265-279.

This paper presents a review of the past decade's highlights of research on the isolation and characterisation of particulate organic matter (POM) in the world's oceans. The emphasis is on chemical studies but, in keeping with the growing interdisciplinary nature of marine science, advances in other disciplines are also discussed, particularly those in biological sciences. Increasing evidence for the importance of picoplankton, bacteria and viruses as POM constituents is highlighted, including the recent recognition of large populations of autotrophic bacteria able to harvest light for energy. The transport of POM to bottom waters was thought to be largely confined to large, rapidly sinking faecal pellets. However, recent studies have highlighted the importance of organic aggregates and floes formed by diatoms such as *Rhizosolenia* and other microalgae. Ascending particles have also been discovered, many of which are lipid-rich. Several studies have shown that resuspension of bottom sediments and lateral advection of material from continental shelves can lead to anomalously high particle fluxes measured in sediment traps moored in deep water. Many new approaches for characterizing POM have emerged, such as pyrolysis gas chromatography-mass spectrometry and direct temperature-resolved mass spectrometry for analysis of higher molecular weight materials and biopolymers. Lipid biomarker techniques have also advanced, exciting new possibilities being raised by the ability to measure stable and radioactive carbon isotopes for individual compounds. The techniques of molecular biology, such as the polymerase chain reaction (PCR), are being increasingly applied to provide complementary information to more conventional microscopy and flow cytometry on the identity of organisms in the sea. The combination of these techniques with advanced chemical analysis methods promises to greatly increase our knowledge of the origins, transport and fate of organic matter in the oceans.

Walker, N. D. and N. N. Rabalais (2006). "Relationships among satellite chlorophyll a, river inputs, and hypoxia on the Louisiana continental shelf, gulf of Mexico." Estuaries and Coasts **29**(6B): 1081-1093.

SeaWiFS ocean color measurements were used to investigate interannual,

monthly, and weekly variations in chlorophyll a (chl a) on the Louisiana shelf and to assess relationships with river discharge, nitrate load, and hypoxia. During the study period (2000-2003), interannual changes in shelf-wide chl a concentrations averaged over January-July ranged from +57% to - 33% of the 4-yr average, in accord with freshwater discharge changes of +20% to - 29% and nitrate load changes of +20% to -35% from the Mississippi and Atchafalaya Rivers. Chl a variations were largest on the shelf between the Mississippi and Atchafalaya Deltas. Within this region, which corresponds spatially to the area of most frequent hypoxia, lowest January-July mean chl a concentrations (5.5 mg m⁻³ over 7,000 km²) occurred during 2000, the year of lowest freshwater discharge (16,136 m³ s⁻¹) and nitrate load (55,738 MT N d⁻¹) onto the shelf. Highest January-July mean chl a concentrations (13 mg m⁻³ over 7,000 km²) were measured in 2002, when freshwater discharge (27,440 m³ s⁻¹) and nitrate load (101,761 MT N d⁻¹) were highest and second highest, respectively. Positive correlations ($R^2 = 0.4-0.5$) were found between chl a and both freshwater and nitrate loads with 0 to 1 month lags, with the strongest relationships just west of the Mississippi Delta. In 2001, unusually clear skies allowed the identification of distinct spring and summer chl a blooms west of the Mississippi Delta 4-5 wk after peaks in river discharge. East of the delta, the chl a concentrations peaked in June and July, following the seasonal reversal in the coastal current. A clear linkage was not detected between satellite-measured chl a and hypoxia during the 4-yr period, based on a time series of bottom oxygen concentrations at one station within the area of most frequent hypoxia. Clear relationships are confounded by the interaction of physical processes (wind stress effects) with the seasonal cycle of nutrient-enhanced productivity and are influenced by the prior year's nitrate load and carbon accumulation at the seabed.

Walker, N. D., W. J. Wiseman, et al. (2005). "Effects of river discharge, wind stress, and slope eddies on circulation and the satellite-observed structure of the Mississippi River plume." Journal of Coastal Research **21**(6): 1228-1244.

Satellite measurements of suspended sediment, temperature, and chlorophyll a are used in combination with surface current measurements to investigate surface circulation and structure of the Mississippi River plume. River discharge changes affect frontal locations, areal extent, and suspended sediment loads of the plume. During high river discharge ($> 20,000 \text{ m}^3 \text{ s}^{-1}$) in spring, the sediment plume extends 23 km southwestward, covers 2700 km², with maximum concentrations of 360 mg L⁻¹. Plume temperatures vary seasonally from 10 degrees to 28 degrees C, with maximum surface fronts of 3.3 degrees C km⁻¹ in winter. East winds, prevalent in autumn, winter, and spring, drive a westward flow of river waters around the delta, linking two isolated shelf regions and increasing river discharge onto the Louisiana/Texas shelf. During peak river flow, this westward current exhibits velocities of 40-90 cm s⁻¹, is 20 km wide, and transports 140,000-165,000 m³ s⁻¹ of river and shelf water. It usually turns toward the coast between 89.5 degrees W and 90 degrees W, feeding a clockwise gyre in the Louisiana Bight and a westward coastal current. The

prevalent east winds trap river water and associated nutrients on the shelf where hypoxia later develops in late spring/summer. During autumn and winter, short-term wind reversals from frontal passages rapidly reverse plume direction, initiate off-shelf transport, and reduce residence times for river waters and associated sediments, nutrients, phytoplankton, and carbon. During summer, persistent southwest and south winds force river water eastward, where cross-margin transport is likely due to the relatively narrow shelf. Slope eddies and the Loop Current control river water after leaving the shelf.

Wall, L. G., J. L. Tank, et al. (2005). "Spatial and temporal variability in sediment denitrification within an agriculturally influenced reservoir." Biogeochemistry **76**(1): 85-111.

Reservoirs are intrinsically linked to the rivers that feed them, creating a river - reservoir continuum in which water and sediment inputs are a function of the surrounding watershed land use. We examined the spatial and temporal variability of sediment denitrification rates by sampling longitudinally along an agriculturally influenced river - reservoir continuum monthly for 13 months. Sediment denitrification rates ranged from 0 to 63 $\mu\text{g N}_2\text{O g ash free dry mass of sediments (AFDM)}^{-1} \text{ h}^{-1}$ or 0 - 2.7 $\mu\text{g N}_2\text{O g dry mass of sediments (DM)}^{-1} \text{ h}^{-1}$ at reservoir sites, vs. 0 - 12 $\mu\text{g N}_2\text{O gAFDM}^{-1} \text{ h}^{-1}$ or 0 - 0.27 $\mu\text{g N}_2\text{O gDM}^{-1} \text{ h}^{-1}$ at riverine sites. Temporally, highest denitrification activity traveled through the reservoir from upper reservoir sites to the dam, following the load of high nitrate ($\text{NO}_3\text{-N}$) water associated with spring runoff. Annual mean sediment denitri. cation rates at different reservoir sites were consistently higher than at riverine sites, yet significant relationships among these sites differed when denitrification rates were expressed per gDM vs. per gAFDM. There was a significant positive relationship between sediment denitri. cation rates and $\text{NO}_3\text{-N}$ concentration up to a threshold of 0.88 $\text{mg NO}_3\text{-N l}^{-1}$, above which it appeared $\text{NO}_3\text{-N}$ was no longer limiting. Denitrification assays were amended seasonally with $\text{NO}_3\text{-N}$ and an organic carbon source (glucose) to determine nutrient limitation of sediment denitri. cation. While organic carbon never limited sediment denitrification, all sites were significantly limited by $\text{NO}_3\text{-N}$ during fall and winter when ambient $\text{NO}_3\text{-N}$ was low.

Walsh, J. J. and D. A. Dieterle (1994). "CO₂ CYCLING IN THE COASTAL OCEAN .1. A NUMERICAL-ANALYSIS OF THE SOUTHEASTERN BERING SEA WITH APPLICATIONS TO THE CHUKCHI SEA AND THE NORTHERN GULF-OF-MEXICO." Progress in Oceanography **34**(4): 335-392.

A quasi-two dimensional model of the carbon and nitrogen cycling above the 70m isobath of the southeastern Bering Sea at 57-degrees-N replicates the observed seasonal cycles of nitrate, ammonium, SIGMACO_2 , pCO_2 , light penetration, chlorophyll, phytoplankton growth rate, and primary production, as constrained by changes in wind, incident radiation, temperature, ice cover, vertical and lateral mixing, grazing stress, benthic processing of phytodetritus and zooplankton fecal pellets, and the pelagic microbial loop of DOC, bacteria, and their predators. About half of the seasonal resupply of nitrate stocks to their

initial winter conditions is derived from in situ nitrification, with the rest obtained from deep-sea influxes. Under the present conditions of atmospheric forcing, shelf-break exchange, and food web structure, this shelf ecosystem serves as a sink for atmospheric CO₂, with storage in the forms of exported DOC, DIC, and unutilized POC (phytoplankton, bacteria, and fecal pellets). As a consequence of just the rising levels of atmospheric pCO₂ since the Industrial Revolution, however, the biophysical CO₂ status of the Southeastern Bering Sea shelf may have switched over the last 250 years, from a prior source to the present sink, since this relatively pristine ecosystem has undergone little eutrophication. Such fluctuations of CO₂ status may thus be reversed by the physical processes of: (1) reduction of atmospheric pCO₂, (2) increased onwelling of deep-sea SIGMACO₂, and (3) warming of shelf waters. Based on our application of this model to the Chukchi Sea and the Gulf of Mexico, about 1.0-1.2 gigatons C y⁻¹ of atmospheric CO₂ may now be sequestered by temperate and polar shelf ecosystems. When tropical systems are included, however, a positive net sink of only 0.6-0.8 x 10¹⁵g C y⁻¹ may prevail over all shelves.

Walsh, J. J., R. H. Weisberg, et al. (2003). "Phytoplankton response to intrusions of slope water on the West Florida Shelf: Models and observations." Journal of Geophysical Research-Oceans **108**(C6).

Previous hypotheses had suggested that upwelled intrusions of nutrient-rich Gulf of Mexico slope water onto the West Florida Shelf (WFS) led to formation of red tides of *Karenia brevis*. However, coupled biophysical models of (1) wind- and buoyancy-driven circulation, (2) three phytoplankton groups (diatoms, *K. brevis*, and microflagellates), (3) these slope water supplies of nitrate and silicate, and (4) selective grazing stress by copepods and protozoans found that diatoms won in one 1998 case of no light limitation by colored dissolved organic matter (CDOM). The diatoms lost to *K. brevis* during another CDOM case of the models. In the real world, field data confirmed that diatoms were indeed the dominant phytoplankton after massive upwelling in 1998, when only a small red tide of *K. brevis* was observed. Over a 7-month period of the CDOM-free scenario the simulated total primary production of the phytoplankton community was similar to 1.8 g C m⁻² d⁻¹ along the 40-m isobath of the northern WFS, with the largest accumulation of biomass on the Florida Middle Ground (FMG). Despite such photosynthesis, these models of the WFS yielded a net source of CO₂ to the atmosphere during spring and summer and suggested a small sink in the fall. With diatom losses of 90% of their daily carbon fixation to herbivores the simulation supported earlier impressions of a short, diatom-based food web on the FMG, where organic carbon content of the surficial sediments is tenfold those of the surrounding seabeds. Farther south, the simulated near-bottom pools of ammonium were highest in summer, when silicon regeneration was minimal, leading to temporary Si limitation of the diatoms. Termination of these upwelled pulses of production by diatoms and nonsiliceous microflagellates mainly resulted from nitrate exhaustion in the model, however, mimicking most del¹⁵PON observations in the field. Yet, the CDOM-free case of the models failed to replicate the observed small red tide in December 1998, tagged with the

del(¹⁵N) signature of nitrogen fixation. A large red tide of *K. brevis* did form in the CDOM-rich case, when estuarine supplies of CDOM favored the growth of the shade-adapted, ungrazed dinoflagellates. The usual formation of large harmful algal blooms of >1 ug chl L⁻¹ (10⁵ cells L⁻¹) in the southern part of the WFS, between Tampa Bay and Charlotte Harbor, must instead depend upon local aeolian and estuarine supplies of nutrients and CDOM sun screen, not those from the shelf break. In the absence of slope water supplies, local upwelling instead focuses nitrate-poor inocula of co-occurring *K. brevis* and nitrogen fixers at coastal fronts for both aggregation and transfer of nutrients between these phytoplankton groups.

Wang, X. C., R. F. Chen, et al. (2004). "Sources and transport of dissolved and particulate organic carbon in the Mississippi River estuary and adjacent coastal waters of the northern Gulf of Mexico." Marine Chemistry **89**(1-4): 241-256.

Dissolved organic carbon (DOC), stable carbon isotopic ($\delta^{13}\text{C}$) compositions of DOC and particulate organic carbon (POC), and elemental C/N ratios of POC were measured for samples collected from the lower Mississippi and Atchafalaya rivers and adjacent coastal waters in the northern Gulf of Mexico during the low flow season in June 2000 and high flow season in April 2001. These isotopic and C/N results combined with DOC measurements were used to assess the sources and transport of terrestrial organic matter from the Mississippi and Atchafalaya rivers to the coastal region in the northern Gulf of Mexico. $\delta^{13}\text{C}$ values of both POC (-23.8parts per thousand to -26.8parts per thousand) and DOC (-25.0parts per thousand to -29.0parts per thousand) carried by the two rivers were more depleted than the values measured for the samples collected in the offshore waters. Strong seasonal variations in $\delta^{13}\text{C}$ distributions were observed for both POC and DOC in the surface waters of the region. Fresh water discharge and horizontal mixing played important roles in the distribution and transport of terrestrial POC and DOC offshore. Our results indicate that both POC and DOC exhibited non-conservative behavior during the mixing especially in the mid-salinity range. Based on a simple two end-member mixing model, the comparison of the measured DOC- $\delta^{13}\text{C}$ with the calculated conservative isotopic mixing curve indicated that there was a significant in situ production of marine-derived DOC in the mid- to high-salinity waters consistent with our in situ chlorophyll-a measurements. Our DOC- $\delta^{13}\text{C}$ data suggest that a removal of terrestrial DOC mainly occurred in the high-salinity (>25) waters during the mixing. Our study indicates that the mid- to high- (10-30) salinity range was the most dynamic zone for organic carbon transport and cycling in the Mississippi River estuary. Variability in isotopic and elemental compositions along with variability in DOC and POC concentrations suggest that autochthonous production, bacterial utilization, and photo-oxidation could all play important roles in regulating and removing terrestrial DOC in the northern Gulf of Mexico and further study of these individual processes is warranted. (C) 2004 Elsevier B.V. All rights reserved.

Wang, X. C., R. F. Chen, et al. (2001). "Contribution of "old" carbon from natural marine hydrocarbon seeps to sedimentary and dissolved organic carbon pools in the Gulf of Mexico." Geophysical Research Letters **28**(17): 3313-3316.

Natural radiocarbon (C-14) abundances and stable carbon isotope (δ C-13) compositions were measured for sediment total organic carbon (TOC), and total lipid fractions of sediments, bottom water, and hydrate-water collected from two hydrocarbon seepage sites in Green Canyon, Northern Gulf of Mexico to determine the contribution of "old" carbon from seeps to sediment TOC and dissolved organic carbon (DOC) pools. Our results indicate that 40-60% of the organic carbon preserved in the sediments and 30% of the DOC in the deep water above the seeps were seep-derived C-14-depleted organic carbon. This new evidence along with our previous studies suggest that natural marine hydrocarbon seepage could be a significant source contributing "old" carbon to the marine environment. Our findings suggest that the global importance and the long-term impact of this contribution to biogeochemical carbon cycling in the ocean need to be more thoroughly investigated.

Wawrik, B. and J. H. Paul (2004). "Phytoplankton community structure and productivity along the axis of the Mississippi River plume in oligotrophic Gulf of Mexico waters." Aquatic Microbial Ecology **35**(2): 185-196.

The Mississippi River is the largest freshwater input into the Gulf of Mexico (GOM) and contributes a large nutrient load to northern GOM waters. During the summer, the Mississippi River plume is sometimes found to extend into the eastern oligotrophic GOM as far as the Dry Tortugas. The objectives of this study were to determine the relative contribution of the Mississippi River plume to the total surface water production in the oligotrophic GOM and the impact of this feature on the composition of phytoplankton found there. Using Sea-viewing Wide Field-of-View Sensor (SeaWiFS) satellite images, we located and sampled the offshore Mississippi plume along its axis. In situ sampling in combination with remote sensing allowed us to estimate integrated plume primary productivity. Carbon fixation in the northern GOM averaged $0.53 \mu\text{g C l}^{-1} \text{ h}^{-1}$ for non-plume stations, and $9.3 \text{ Pg C l}^{-1} \text{ h}^{-1}$ in plume stations. We estimated integrated productivity of the plume at ca. $3.28 \times 10^9 \text{ g C h}^{-1}$, which accounted for 41 and 13% of all surface and total water column productivity in the oligotrophic GOM, respectively, at the time of sampling. Analysis of *rbcl* cDNA clone libraries and HPLC pigment data indicated that our sampling transect traversed several regions with distinctly different phytoplankton assemblages. Non-plume communities were numerically dominated by *Prochlorococcus*, and contained prymnesiophytes and eustigmatophytes. Diatoms dominated the most productive inshore station, while *Synechococcus* dominated in the mid-plume just off the Louisiana shelf. The least productive and most offshore portion of the plume was also diatom dominated. Diatoms were the most diverse algal class observed, accounting for over 42% of all unique *rbcl* genotypes detected in the plume. Collectively, these results indicate that the Mississippi River plume contributes significantly to oligotrophic productivity in the GOM, resulting from localized blooms of both *Synechococcus* and diatoms.

Wawrik, B., J. H. Paul, et al. (2004). "High rates of ammonium recycling drive phytoplankton productivity in the offshore Mississippi River plume." Aquatic Microbial Ecology **35**(2): 175-184.

As part of an integrated study of the regulation of carbon fixation in the offshore Mississippi River plume, we measured the rates of N-15-labeled ammonium and nitrate uptake in the surface plume waters from offshore to nearshore along the plume axis towards the Mississippi Delta. Concentrations of nitrate in the plume ranged from 0.19 to 2.5 μM with the highest concentrations primarily in the shoreward stations, while ammonium ranged from 0.17 to 0.44 μM , showing little spatial variability. Rates of ammonium uptake ranged from 16.5 to 260 nM h^{-1} , and showed a strong trend of increasing values from offshore towards the Mississippi Delta. In contrast, nitrate uptake rates ranged from 3.2 to 25 nM h^{-1} . The high rates of ammonium uptake in the presence of low ammonium concentrations and elevated nitrate was made possible by elevated rates of ammonium regeneration that exceeded ammonium uptake by 1.7 to 5.7-fold in the plume. The plume exhibited relatively low f-ratios and also contained elevated levels of *Synechococcus* as determined by flow cytometry and high levels of form IA (alpha-cyanobacterial) *rbcL* transcripts. These data suggest that a major portion of the carbon fixation observed in the offshore Mississippi River plume represents recycled production supported by high rates of ammonium regeneration.

Wawrik, B., J. H. Paul, et al. (2003). "Vertical structure of the phytoplankton community associated with a coastal plume in the Gulf of Mexico." Marine Ecology-Progress Series **251**: 87-101.

Low salinity plumes of coastal origin are occasionally found far offshore, where they display a distinct color signature detectable by satellites. The impact of such plumes on carbon fixation and phytoplankton community structure in vertical profiles and on basin wide scales is poorly understood. On a research cruise in June 1999, ocean-color satellite-images (Sea-viewing Wide Field-of-view Sensor, SeaWiFS) were used in locating a Mississippi River plume in the eastern Gulf of Mexico. Profiles sampled within and outside of the plume were analyzed using flow cytometry, HPLC pigment analysis and primary production using C-14 incorporation. Additionally, RubisCO large subunit (*rbcL*) gene expression was measured by hybridization of extracted RNA using 3 full-length RNA gene probes specific for individual phytoplankton clades. We also used a combination of RT-PCR/PCR and TA cloning in order to generate cDNA and DNA *rbcL* clone libraries from samples taken in the plume. Primary productivity was greatest in the low salinity surface layer of the plume. The plume was also associated with high *Synechococcus* counts and a strong peak in Form IA *rbcL* expression. Form IB *rbcL* (green algal) mRNA was abundant at the subsurface chlorophyll maximum (SCM), whereas Form ID *rbcL* (chromophytic) expression showed little vertical structure. Phylogenetic analysis of cDNA libraries demonstrated the presence of Form IA *rbcL* *Synechococcus* phylotypes in the plume. Below the plume, 2 spatially separated and genetically distinct *rbcL* clades of

Prochlorococcus were observed. This indicated the presence of the high- and low-light adapted clades of Prochlorococcus. A large and very diverse clade of Prymnesiophytes was distributed throughout the water column, whereas a clade of closely related prasinophytes may have dominated at the SCM. These data indicate that the Mississippi river plume may dramatically alter the surface picoplankton composition of the Gulf of Mexico, with Synechococcus displacing Prochlorococcus in the surface waters.

Wells, M. L. (2004). "The colloidal size spectrum of CDOM in the coastal region of the Mississippi Plume using flow field-flow fractionation." *Marine Chemistry* **89**(1-4): 89-102. Chromophoric dissolved organic matter (CDOM) is a major component of the total dissolved organic matter in seawater, and it can interfere significantly with oceanographic remote sensing in nearshore waters. Coastal marine CDOM comprises an undefined, likely rapidly changing mixture of terrestrially and marine-derived substances. Flow Field-Flow Fractionation (FIFFF) offers a novel approach for separating the colloidal (high molecular weight) fraction of CDOM into broad size continuums that can offer insights to the characteristics and reactivity of CDOM constituents. FIFFF analyses of seawaters in and around the Mississippi Plume were performed during high and low flow conditions and the results compared to analyses of phytoplankton cultures and waters from a coastal estuary having low freshwater inputs. FIFFF fractograms displayed major differences in the size distribution of CDOM between offshore in the Gulf of Mexico (GOMex) and the Mississippi River plume. Colloidal size distributions in nearshore surface waters out of the immediate influence of the Mississippi Plume contained a mixture of features seen in offshore waters, plume waters, and in phytoplankton cultures. Plume waters had a high abundance of larger colloidal phases but continued dilution with coastal waters led to preferential losses of mid-sized colloidal matter. Colloidal size spectra in offshore waters of the GOMex during spring were similar to that observed in estuarine waters after the spring bloom. These preliminary findings suggest that the colloidal size spectrum of CDOM may provide information on its provenance and the relative mixtures of terrestrial and marine components. (C) 2004 Elsevier B.V. All rights reserved.

Wissel, B., A. Gace, et al. (2005). "Tracing river influences on phytoplankton dynamics in two Louisiana estuaries." *Ecology* **86**(10): 2751-2762.

To evaluate effects of river inputs on estuarine phytoplankton, we compared particulate organic matter (POM) dynamics in two neighboring estuaries from the Mississippi River delta. The two estuaries, Barataria Basin and Breton Sound, have been isolated from the Mississippi River at their upstream ends for most of the last century due to levee construction, but for the last 13 years, Breton Sound has been reconnected to the Mississippi River via a gated diversion at Caernarvon, Louisiana. Thus, Barataria Basin was the reference estuary and Breton Sound was the river-impacted estuary. We focused on POM because it was relatively easy to collect and analyze, and because POM dynamics gave a good ecosystem-level overview of phytoplankton responses to riverine nutrient forcing and hydrologic forcing. A combination of C:N and (POC)-C-13 analyses

indicated that most POM was phytoplankton with smaller contributions of sediment. Estuarine concentrations of particulate organic carbon (POC) and nitrogen (PON) were typically higher than end-member freshwater or marine inputs, indicating the importance of within-system phytoplankton growth likely fueled by rapid nutrient regeneration in these warm, shallow and well-mixed estuarine systems. Isotopic analyses generally showed typical estuarine gradients in the reference Barataria Basin estuary, but the river-influenced upper Breton Sound had elevated (POC)-C-13 and (PON)-N-15 values useful for following the spatial extent of river impacts. Rapid river-assisted flushing in Breton Sound probably prevented widespread development of algal blooms in response to introductions of the nutrient-rich river water, but study of some isolated lakes suggested that when longer residence times apply, introduction of river water to coastal estuaries can lead to eutrophic conditions and in some cases, harmful algal blooms. Overall, routinely monitoring amounts and isotopic compositions of POM proved an effective way to trace linkages between river inputs and downstream estuarine phytoplankton dynamics.

Wysocki, L. A., T. S. Bianchi, et al. (2006). "Spatial variability in the coupling of organic carbon, nutrients, and phytoplankton pigments in surface waters and sediments of the Mississippi River plume." Estuarine Coastal and Shelf Science **69**(1-2): 47-63.

River-dominated coastal areas are typically sites of active biogeochemical cycling, with productivity enhanced by terrestrial inputs of nutrients and organic matter. To examine the spatial variability and relationship between river discharge, phytoplankton, and organic carbon distributions, we analyzed surface water and sediment from the Louisiana shelf adjacent to the Mississippi River. Samples were collected during April and October 2000 to capture high and low river discharge, and were analyzed for dissolved and particulate organic carbon (DOC and POC), nutrients, and phytoplankton pigments. Pigments, determined by high performance liquid chromatography (HPLC), were also analyzed from sediment to evaluate marine carbon inputs to the seafloor. DOC in surface waters was generally within 200-300 μM , ranging up to 399 μM . Chlorophyll a ranged from below the limits of detection (BLD) up to 31 nM in surface waters, with higher values located further from the river mouth during high flow. Although community diversity increased during low discharge, diatoms dominated the phytoplankton population (50-80% of the community throughout the study) and consequently made more important contributions than other species to both the DOC and POC pools. Chlorophyll and degradation products (indicative of zooplankton grazing) observed in surface sediment indicated a transfer of autochthonous carbon from the highly productive photic zone to the sediment, coupling phytoplankton-derived POC in surface waters with organic carbon deposition in surface sediment. Cross-shelf changes in chlorophyll indicated a westward transport of phytoplankton that was directly and indirectly linked with river discharge and pigment decay dynamics. (c) 2006 Elsevier Ltd. All rights reserved.

Yeager, K. M., P. H. Santschi, et al. (2004). "Sediment accumulation and radionuclide

inventories (Pu-239,Pu-240, Pb-210 and Th-234) in the northern Gulf of Mexico, as influenced by organic matter and macrofaunal density." Marine Chemistry **91**(1-4): 1-14.

Six cores were collected from the Northern Gulf of Mexico (GOM) as part of the "Deepwater Program: Northern Gulf of Mexico Continental Slope Habitats and Benthic Ecology" (DGoMB). These cores were collected from water depths ranging from approximate to 700 to 3500 m, and processed for radiochemical assays to determine particle reworking (bioturbation) and sedimentation rates in these sediments, pursuant to the research objective to investigate biological, chemical, and physical processes that control the environmental setting for GOM benthic fauna. Bioturbation rates were quantitatively derived from Th-234(xs) profiles, with Th-234(xs) penetration depths ranging between 0.5 and 4 cm, and bioturbation coefficient values (D-b), ranging from approximate to 2 to 30 cm²/year. Th-234(xs) data were also used to determine the shallow depth limit for particle mixing. Significant values of Pu-239,Pu-240 were found over the 3-15 cm depth range, without any pronounced peak activities suitable for sediment dating, indicating periodic and nonlocal mixing events. Sedimentation rates (S) were therefore calculated from Pb-210(xs) profiles, assuming steady state conditions, and using the constant flux-constant sedimentation (CF-CS) model. However, only Pb-210(xs) data below the Pu-239,Pu-240 penetration depth were used for the purpose of determining an upper limit of S. The range of apparent sedimentation rates determined by this approach for these stations is 0.04-0.44 cm/year, after approximately 1000 m depth, sedimentation becomes essentially constant at approximate to 0.08 cm/year. To the best of our knowledge, there are no other published sedimentation rates for the GOM outside the immediate area of the Mississippi River Delta region. However, estimates of sedimentation rates presented here fall in line with rates from similar continental margin marine settings. Pu-239,Pu-240 and Pb-210(xs) inventories are positively correlated ($r=0.91$, $p=0.01$; $r=0.80$, $p=0.05$, respectively) with macrofauna density, which itself correlates well ($r=0.94$, $p=0.005$) to particulate organic carbon (POC) inventories over the top 5 cm, the approximate average particle mixing (bioturbation) depths of Th-234(xs) at these GOM stations. However, these inventories did not correlate to benthic mixing intensities and depths. High macrofaunal densities and bioturbation intensities are a consequence of elevated rain rates of organic carbon, which is efficiently degraded at the sediment-water interface before incorporation into the sedimentary record. We hypothesize that relatively high densities of macrofauna in a given location on the sea floor, provide for a well mixed near surface sediment layer, wherein fallout radionuclides are more efficiently incorporated via adsorption and mixing into the sediment profile as compared to locations where macrofaunal densities are less, even when radionuclide fluxes might be similar. (C) 2004 Elsevier B.V. All rights reserved.

Zanardi-Lamardo, E., C. D. Clark, et al. (2002). "Comparison of the molecular mass and optical properties of colored dissolved organic material in two rivers and coastal waters by flow field-flow fractionation." Environmental Science & Technology **36**(13): 2806-2814.

Colored dissolved organic material (CDOM) is an important sunlight absorbing substance affecting the optical properties of natural waters. However, little is known about its structural and optical properties mainly due to its complex matrix and the limitation of the techniques available. A comparison of two southwestern Florida rivers [the Caloosahatchee River (CR) and the Shark River (SR)] was done in terms of molecular mass (MM) and diffusion coefficients (D). The novel technique Frit inlet/frit outlet-flow field-flow fractionation (FIFO-FIFFF) with absorbance and fluorescence detectors was used to determine these properties. The SR receives organic material from the Everglades. By contrast, the CR arises from Lake Okeechobee in central Florida, receiving anthropogenic inputs, farming runoff, and natural organics. Both rivers discharge to the Gulf of Mexico. Fluorescence identified, for both rivers, two different MM distributions in low salinity water samples: the first was centered at similar to 1.7 kDa (CR) and similar to 2 kDa (SR); the second centered at similar to 13 kDa for both rivers, which disappeared gradually in the river plumes to below detection limit in coastal waters. Absorbance detected only one MM distribution centered at similar to 2 kDa (CR) and 2.2-2.4 kDa (SR). Fluorescence in general peaked at a lower MM than absorbance, suggesting a different size distribution for fluorophores vs chromophores. A photochemical study showed that, after sunlight, irradiated freshwater samples have similar characteristics to more marine waters, including a shift in MM distribution of chromophores. The differences observed between the rivers in the optical characteristics, MM distributions, and D values suggest that the CDOM sources, physical, and photochemical degradation processes are different for these two rivers.

Zhang, C. L., Z. Y. Huang, et al. (2005). "Lipid biomarkers and carbon isotope signatures of a microbial (*Beggiatoa*) mat associated with gas hydrates in the Gulf of Mexico." Applied and Environmental Microbiology **71**(4): 2106-2112.

White and orange mats are ubiquitous on surface sediments associated with gas hydrates and cold seeps in the Gulf of Mexico. The goal of this study was to determine the predominant pathways for carbon cycling within an orange mat in Green Canyon (GC) block GC 234 in the Gulf of Mexico. Our approach incorporated laser-scanning confocal microscopy, lipid biomarkers, stable carbon isotopes, and 16S rRNA gene sequencing. Confocal microscopy showed the predominance of filamentous microorganisms (4 to 5 μ m in diameter) in the mat sample, which are characteristic of *Beggiatoa*. The phospholipid fatty acids extracted from the mat sample were dominated by 16:1 ω 7c/t (67%), 18:1 ω 7c (17%), and 16:0 (8%), which are consistent with lipid profiles of known sulfur-oxidizing bacteria, including *Beggiatoa*. These results are supported by the 16S rRNA gene analysis of the mat material, which yielded sequences that are all related to the vacuolated sulfur-oxidizing bacteria, including *Beggiatoa*, *Thioploca*, and *Thiomargarita*. The $\delta(13)\text{C}$ value of total biomass was -28.6‰; those of individual fatty acids were -29.4 to -33.7‰. These values suggested heterotrophic growth of *Beggiatoa* on organic substrates that may have $\delta(13)\text{C}$ values characteristic of crude oil or on their by-products from microbial degradation. This study demonstrated that integrating lipid biomarkers,

stable isotopes, and molecular DNA could enhance our understanding of the metabolic functions of *Beggiatoa* mats in sulfide-rich marine sediments associated with gas hydrates in the Gulf of Mexico and other locations.

Zhang, C. L., R. D. Pancost, et al. (2003). "Archaeal lipid biomarkers and isotopic evidence of anaerobic methane oxidation associated with gas hydrates in the Gulf of Mexico." Organic Geochemistry **34**(6): 827-836.

Anaerobic oxidation of methane (AOM) occurs in the Gulf of Mexico gas hydrate systems. Here we show lipid biomarker and isotopic evidence that archaea are involved in AOM. The estimated abundance of total archaeal lipids ranges from 44.8 to 60.4 $\mu\text{g/g}$ (dry sediment) in hydrate-bearing samples but is below detection limit in the hydrate-free sample. The $\delta^{13}\text{C}$ values of archaeal lipids range from -69 to -99 parts per thousand in hydrate-bearing samples. These results suggest that biomass of archaea is significantly enhanced through AOM at the gas hydrate deposits. These data also support a currently acknowledged mechanism of AOM mediated by a consortium of sulfate-reducing bacteria and archaea observed in a variety of methane-rich marine settings. Anaerobic oxidation of oil hydrocarbons also occurs in the Gulf of Mexico gas hydrate systems as shown by degradation of n-alkanes ($> \text{C-15}$) in the anoxic sediments. These processes convert hydrocarbons to carbon dioxide and increase pore water alkalinity, which promote the precipitation of enormous volumes of authigenic carbonate rock depleted in C-13. This long-term geologic sequestration of carbon may affect models of global climate change. (C) 2003 Elsevier Science Ltd. All rights reserved.

Zhang, C. L., R. Sassen, et al. (2002). "Carbon cycling in the Gulf of Mexico gas hydrate systems: A review." Geochimica Et Cosmochimica Acta **66**(15A): A872-A872.

Zhang, C. L. L., Y. L. Li, et al. (2002). "Lipid and carbon isotopic evidence of methane-oxidizing and sulfate-reducing bacteria in association with gas hydrates from the Gulf of Mexico." Geology **30**(3): 239-242.

An integrated lipid biomarker-carbon isotope approach reveals new insight to microbial methane oxidation in the Gulf of Mexico gas-hydrate system. Hydrate-bearing and hydrate-free sediments were collected from the Gulf of Mexico slope using a research submersible. Phospholipid fatty acids consist mainly of C-16-C-18 compounds, which are largely derived from bacteria. The phospholipid fatty acids suggest that total biomass is enhanced 11-30-fold in gas-hydrate-bearing sediment compared to hydrate-free sediment. Lipid biomarkers indicative of sulfate-reducing bacteria are strongly depleted in C-13 ($\delta^{13}\text{C} = -48\%$ to -70%) in the hydrate-bearing samples, suggesting that they are involved in the oxidation of methane ($\delta^{13}\text{C} = -47\%$ for thermogenic methane and -70% for biogenic methane). Isotopic properties of other biomarkers suggest that sulfur-oxidizing bacteria (*Beggiatoa*) may also contribute to the lipid pool in hydrate-bearing samples, which are characterized by less negative $\delta^{13}\text{C}$ values (to -11.2%). In the hydrate-free sample, fatty acid biomarkers have $\delta^{13}\text{C}$ values of -27.6% to -39.6% , indicating that

crude oil (average similar to-27‰) or terrestrial organic carbon (average similar to-20‰) are the likely carbon sources. Our results provide the first lipid biomarker-stable isotope evidence that sulfate-reducing bacteria play an important role in anaerobic methane oxidation in the Gulf of Mexico gas hydrates. The coupled activities of methane-oxidizing and sulfate-reducing organisms contribute to the development of ecosystems in deep-sea environments and result in sequestration of carbon as buried organic carbon and authigenic carbonates. These have implications for studying climate change based on carbon budgets.

Zimmerman, A. R. and R. Benner (1994). "DENITRIFICATION, NUTRIENT REGENERATION AND CARBON MINERALIZATION IN SEDIMENTS OF GALVESTON BAY, TEXAS, USA." Marine Ecology-Progress Series **114**(3): 275-288.

Rates of benthic denitrification, oxygen consumption and nutrient regeneration were measured during winter, spring and summer in Galveston Bay (Texas, USA) sediments. Denitrification ranged from 0 to 47 $\mu\text{mol N}^{-2} \text{m}^{-2} \text{h}^{-1}$ with maximal rates generally occurring in the summer and the upper estuary. Oxygen consumption rates ranged from 38 $\mu\text{mol O}_2 \text{m}^{-2} \text{h}^{-1}$ in the winter to 353 $\mu\text{mol O}_2 \text{m}^{-2} \text{h}^{-1}$ in the summer and were correlated with denitrification rates. Variations in bay water temperature accounted for 52 % of the variability associated with denitrification rates whereas only 28 % of the variability could be attributed to organic carbon content and 15% to salinity, indicating a predominance of temporal over spatial factors in controlling estuarine rates of denitrification. In the spring and summer, denitrification was responsible for the majority (73 and 80 %, respectively) of the total benthic inorganic nitrogen efflux while in the winter, nitrogen fluxes were dominated (80 %) by ammonium. At salinities less than 6 parts per thousand, cation exchange interactions may have played an important role in retaining ammonium in the sediment, producing the higher rates of denitrification found in the upper estuary. Dissolved inorganic carbon flux was used as a measure of total organic carbon mineralization. The average molar C:N of the remineralized substrate (5.2) was lower than the average C:N of the sediments (12.6) indicating preferential remineralization of nitrogen relative to carbon. Molar C:O ratios suggested that anaerobic carbon mineralization and the storage of its reduced end-products is more prevalent in the lower estuary and in the winter. Denitrifiers were responsible for 37 and 13 % of the total benthic carbon mineralization in the upper and lower estuary, respectively. Denitrification appears to be a greater contributor to total carbon mineralization than previously considered. Nearly one-third of the total sediment oxygen consumption was attributed to nitrification. Galveston Bay sediment denitrification and oxygen consumption rates and nutrient fluxes were lower but comparable to those of other Gulf of Mexico estuaries. Differences among the estuaries examined are attributed mainly to sediment organic matter content.