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The Lability of Riverine Particulate Organic Carbon Delivered to the Ocean

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Final Report for Period: 01/2006 - 12/2006**Submitted on:** 03/07/2007**Principal Investigator:** Mayer, Lawrence M.**Award ID:** 0223383**Organization:** University of Maine**Title:**

The Lability of Riverine Particulate Organic Carbon Delivered to the Ocean

Project Participants**Senior Personnel****Name:** Mayer, Lawrence**Worked for more than 160 Hours:** Yes**Contribution to Project:****Post-doc****Graduate Student****Name:** Wagai, Rota**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Laboratory assistance

Undergraduate Student**Technician, Programmer****Name:** Schick, Linda**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Laboratory assistance

Name: Hardy, Kathy**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Laboratory assistance

Other Participant**Research Experience for Undergraduates****Organizational Partners****Other Collaborators or Contacts**

Mead Allison, Tulane Univ., collaborated with sediment collection

Sam Bentley, Louisiana State Univ., collaborated with sediment collection

Activities and Findings**Research and Education Activities:**

I collected samples from the Mississippi River and Louisiana shelf regions and analyzed them for various parameters relating to carbon cycling.

I performed various experiments and methods developments efforts to determine the nature of samples and the processes that affect them in the field.

Findings:

1. Photodissolution is a potentially effective reaction by which particulate organic carbon may be mobilized from riverine sediments delivered to the coastal zone.
2. Various parameters controlling photodissolution were studied and their influence quantified.
3. Carbon loss begins in the lower Mississippi river and then occurs quickly after deposition in the nearshore environment.
4. Bromine:organic carbon ratios are useful to determine the relative amounts of marine vs. terrigenous organic matter in the coastal sediments.
5. Reduction of riverine iron oxides causes release of dissolved organic carbon, but this loss is not a major portion of the total loss of organic matter in the coastal zone.

Training and Development:

One graduate student received training in methods development.

An REU student (Krysia Skorko) received training in experimental methods.

Outreach Activities:

I wrote articles and made public presentations (including K-12 classes) about the newly discovered photodissolution reaction and its relationship with global carbon cycling.

Journal Publications

Mayer, L.M., L. Schick, K. Skorko, and E. Boss, "Photodissolution of particulate organic matter from sediments", *Limnology and Oceanography*, p. 1064, vol. 51, (2006). Published

Wagai, R. and L.M. Mayer, "Sorptive stabilization of organic matter in soils by hydrous iron oxides", *Geochimica et Cosmochimica Acta*, p. 25, vol. 71, (2007). Published

Mayer L.M. L. L. Schick, M. Allison, K. Ruttenberg, and S. Bentley, "Marine vs. terrigenous organic matter in Louisiana coastal sediments: The uses of Bromine:organic carbon ratios", *Marine Chemistry*, p. , vol. , (). Submitted

Books or Other One-time Publications

Web/Internet Site

Other Specific Products

Contributions

Contributions within Discipline:

My findings help constrain and orient research into the major loss of organic carbon that occurs at the mouth of large deltaic systems. A new reaction pathway has been discovered, and other reaction pathways have been explored.

Contributions to Other Disciplines:

The photodissolution reaction should be important in other ecosystems. My work has directly led to a proposal to study this same reaction in soil environments, where it may be even more significant than in deltas.

Contributions to Human Resource Development:

Two REU students received exposure to marine sciences, and one has chosen to pursue graduate study in the environmental sciences.

Three graduate students participated in various phases of the research, although only one received direct stipend support. The other two students have continued their graduate careers in areas related to the grant's objectives, albeit with other funding.

Contributions to Resources for Research and Education:

We have built an experimental capability (instrumentation, etc.) to do photochemical work at the University of Maine.

Contributions Beyond Science and Engineering:

The manufacturer of our solar simulator commissioned a trade article based on our work.

Categories for which nothing is reported:

Organizational Partners

Any Book

Any Web/Internet Site

Any Product

“The Lability of Riverine Particulate Organic Carbon Delivered to the Ocean”

This project studied particulate organic carbon (POC) loss from suspended sediment (SPM) delivered by the Mississippi River to the Gulf of Mexico. We addressed three mechanisms for organic matter loss – photodissolution, release from iron oxyhydroxides, and decay of inherently bioavailable organic matter. We studied these processes via laboratory experiments and fieldwork.

We sought the location of POC loss by examining areas lacking reported coverage. This search focused on changes in the lower river basin, where low-flow conditions cause temporary sediment storage in the river channel, and in very shallow nearshore areas where much of the river SPM settles quickly. We tested for loss in the lower river channel by seasonally sampling SPM at St. Francisville and at the mouth of the river in Venice. In almost all samplings the grain size-normalized POC content (as POC:surface area, or OC:SFA, ratio) decreased downriver, suggesting either loss from conservatively transported particles or mixing with deposited sediment having lower OC:SFA values (which would implicate POC loss in channel bed sediments). Cores taken just outside the mouths of the Atchafalaya and Mississippi Rivers in their respective deltas showed significant downcore decreases in OC:SFA from values typical of riverine SPM to ones typical of more distal shelf sediments. While some of this POC loss may result from winnowing of vascular plant detritus (Gordon and Goñi, 2004), we deduce metabolism of nonvascular detritus from similar drops in nitrogen:SFA ratios, which are much less affected by winnowing. These field data imply that POC loss occurs very close to the river-ocean interface in this system.

Photochemical reactions on particulates occupied much of our effort. In irradiation experiments in a solar simulator, we found dissolution of tens of percent of the POC after several days of exposure to strong sunlight (Mayer et al., 2006). Water chemistry (e.g., salinity, nitrate) and SPM isolation and preservation methods were tested extensively; they have little effect on the extent of this reaction, as did iron oxyhydroxide removal. Under constant irradiation conditions a seasonal set of river SPM samples all showed the same dissolution extent. Temperature, on the other hand, may be a strong controlling parameter. Both UV and visible wavelengths can drive this reaction. A hyperbolic response of reaction extent to light dosage allows significant reaction to occur in highly turbid suspensions, despite light penetration into the suspensions of only mm to cm as determined by actinometry (Jankowski et al., 1999). Photodissolution released DOM with higher C:N ratios than that of POM. Our data do not yet allow quantitation of this reaction's contribution to POC loss between the Mississippi river and its depocenter, but they do argue against significant reaction during river flow (river is too deep and turbid and times are too short to allow adequate photon flux) and instead point to its potential significance under nearshore resuspension regimes. More importantly, these results point to a heretofore ignored role for photodissolution of POM at the earth's surface, with interesting implications for a variety of environments.

We examined the nutritional quality, or lability, of riverine POC by analyzing plant pigments and enzymatically hydrolysable amino acids (EHAA – Mayer et al., 1995). Both were quite high - the latter up to 5 mg/g - and well above levels in surficial marine sediments under shallow productive water columns. Accordingly, incubation experiments showed metabolic loss of POC in riverine SPM of up to 10-20% over several

weeks. Agitating sediments had no effect on the extent of loss. Freshly deposited mud collected just outside river mouths showed lower EHAA values and active colonization by benthic invertebrates, indicating important food web subsidy by river SPM and rapid decay of labile material. A manuscript on these changes is in preparation.

To test the role of iron oxyhydroxides (FeOx) we developed a citrate-free version of the classical dithionite extraction, measuring the OC released from reducible FeOx. Less than 4% of the total POC was thus held in riverine SPM, similar to soils from the Mississippi watershed (**Wagai and Mayer, 2007**). This bound OC decreased offshore, indicating reductive release in nearshore sediments. The reaction may have significance for DOC dynamics, but contributes little to the POC loss.

We used bromine:organic carbon ratios to address the controversy over sources of OC in these shelf sediments (**Mayer et al., in review**). Br:OC ratios are distinctly different for terrestrial and marine organic matter (Mayer et al., 1981). Low ratios throughout the lower river and shelf regions corroborate Goñi et al.'s (1998) argument that carbon isotope ratios previously interpreted as marine instead indicate an isotopically enriched residue of terrestrial organic matter. Very little marine organic matter appears to be buried in Mississippi shelf sediments, despite large inputs from the water column. Sites with elevated Br:OC ratios at the sediment-water interface showed drops downcore, consistent with preferential metabolism of marine organic matter. A manuscript on this release in the marine environment is in preparation.

From these field and laboratory results we cannot yet quantitate the processes responsible for POC loss at this river-ocean transition. Loss likely proceeds from a complex of causes rather than a silver bullet. Reductive dissolution of OC from FeOx is minor, and biological decay can explain perhaps tens of percent of that remaining. The latter may be even more important under conditions of cometabolism with marine algal inputs (Aller, 1998). Our data suggest that photodissolution of POC could contribute as much as most of the overall POC loss before burial (see below).

Mayer, L.M., L. Schick, K. Skorko, and E. Boss, 2006. Photodissolution of particulate organic matter from sediments, *Limnology and Oceanography*, 51:1064-1071.

Wagai, R. and L.M. Mayer, 2007. Sorptive stabilization of organic matter in soils by hydrous iron oxides. *Geochimica et Cosmochimica Acta*, 71:25-35.

Mayer L.M. L. L. Schick, M. Allison, K. Ruttenberg, and S. Bentley. Marine vs. terrigenous organic matter in Louisiana coastal sediments: The uses of Bromine:organic carbon ratios, in revision for *Marine Chemistry*.