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Photodissolution of Sedimentary Organic Matter

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Final Report for Period: 09/2010 - 06/2011

Submitted on: 08/02/2011

Principal Investigator: Mayer, Lawrence M.

Award ID: 0623331

Organization: University of Maine

Submitted By:

Mayer, Lawrence - Principal Investigator

Title:

Photodissolution of Sedimentary Organic Matter

Project Participants

Senior Personnel

Name: Mayer, Lawrence

Worked for more than 160 Hours: Yes

Contribution to Project:

Name: SCHICK, LINDA

Worked for more than 160 Hours: No

Contribution to Project:

Ms. Schick retired in the summer of 2007.

Post-doc

Graduate Student

Name: Estapa, Margaret

Worked for more than 160 Hours: Yes

Contribution to Project:

Designed, performed, and interpreted laboratory experiments, analyses and models as part of her PhD thesis

Undergraduate Student

Name: Kendall, Jenna

Worked for more than 160 Hours: No

Contribution to Project:

General laboratory assistance

Name: Schramski, Erin

Worked for more than 160 Hours: No

Contribution to Project:

General laboratory assistance

Technician, Programmer

Name: Thornton, Kathleen

Worked for more than 160 Hours: Yes

Contribution to Project:

Performed laboratory experiments and analyses

Other Participant

Research Experience for Undergraduates

Organizational Partners

The Texas A&M University System

Helped with analyses

Other Collaborators or Contacts

Dr. Neil Blough, University of Maryland. Served as thesis committee member for Margaret Estapa.

Dr. Emmanuel Boss, University of Maine, Served as co-advisor for Margaret Estapa and participated in publications

Activities and Findings

Research and Education Activities:

Activities and findings are described in attached file 'FinalReptFindings'.

Findings: (See PDF version submitted by PI at the end of the report)

Activities and findings are described in attached file 'FinalReptFindings'.

Training and Development:

Training is described in attached file 'FinalReptFindings'.

Outreach Activities:

See attached Findings file.

Journal Publications

Mayer, L.M. L.L., Schick, T. S. Bianchi, and L.A. Wysocki, "Photochemical changes in chemical markers of sedimentary organic matter source and age", *Marine Chemistry*, p. 123, vol. 119, (2008). Published,

Mayer, L.M. L.L., Schick, K.R. Hardy, and M.L. Estapa, "Photodissolution and other photochemical changes upon irradiation of algal detritus", *Limnology and Oceanography*, p. 168, vol. 54, (2009). Published,

Estapa, M.L. and L.M. Mayer, "Photooxidation of particulate organic matter, carbon/oxygen stoichiometry, and related photoreactions", *Marine Chemistry*, p. , vol. 122, (2010). Published,

Mayer, L.M., K.H. Thornton, and L.L. Schick, "Bioavailability of organic matter photodissolved from coastal sediments", *Aquatic Microbial Ecology*, p. , vol. , (2011). Accepted,

Estapa, M.L., E. Boss, L.M. Mayer, and C.R. Roesler, "Role of iron and organic carbon in mass-specific light absorption by particulate matter from Louisiana coastal waters", *Limnology and Oceanography*, p. , vol. , (2011). Accepted,

Books or Other One-time Publications

Web/Internet Site

Other Specific Products

Contributions

Contributions within Discipline:

Extended our understanding of the photochemistry of particulates in the ocean, especially as it relates to carbon cycling issues.

Contributions to Other Disciplines:

Our findings on the bioavailability of photodissolved organic matter, as well as photochemistry of algal detritus, should be of interest to the field of planktonic microbial ecology.

We did preliminary experiments to examine the possibility of photodissolution of soil organic matter, subsequently received an exploratory grant to further these studies, and currently have a paper in review demonstrating this process.

Contributions to Human Resource Development:

One graduate student - Margaret Estapa - worked on this project and focused her thesis on its central themes. She has developed skills in project design, execution and interpretation. She successfully defended and has embarked on a post-doc at Woods Hole using skills developed from this thesis work. She will be a very successful scientist, in my opinion.

Contributions to Resources for Research and Education:

We have purchased and installed an integrating sphere, which expands our optical instrumentation infrastructure.

Contributions Beyond Science and Engineering:

Conference Proceedings

Categories for which nothing is reported:

Any Book

Any Web/Internet Site

Any Product

Contributions: To Any Beyond Science and Engineering

Any Conference

Several chemical markers of organic matter source and age were shown to be susceptible to light-induced alteration. To test for the photochemical lability of markers previously employed for sediments from the Louisiana coastal zone, we subjected sediments under resuspension conditions to simulated sunlight, and monitored changes in C:N and Br:OC ratios, $\delta^{13}\text{C}$, $\delta^{14}\text{C}$, and lignin composition. Markers of terrigenous origin (high C:N, lignin) decreased and $\delta^{13}\text{C}$ became enriched in sediments containing primarily terrigenous organic matter, while a marker of marine organic matter (Br:OC) decreased in samples containing significant contributions from this source. Preferential loss of ^{14}C from all sediments indicated enhanced photochemical lability of organic matter of relatively recent origin, consistent with the changes in chemical markers. Most, but not all, experimental alterations are consistent with field distributions of these markers. Relatively small experimental changes in the markers in combination with confounding processes in the environment, however, prevent these parallel trends from providing any more than a consistency test for the importance of photochemical reactions in this region.

Based on literature pointing toward photoreactivity of phytoplanktonic detritus, we examined effects of irradiation of algal membrane fragments in various stages of decay, with emphasis on transfer of materials from solid to dissolved phase (photodissolution). After simulated solar irradiation for 24 h, up to several tens of percent of particulate organic matter converted to photodissolved organic matter (PDOM). Prior microbial decay enhanced PDOM production. PDOM had initially high C:N ratios which decreased with irradiation time. Dissolved organic nitrogen dominated nitrogen photodissolution, followed by minor photoammonification and negligible nitrite plus nitrate production. Chromophoric particulate organic matter bleached at visible wavelengths and underwent dissolution, creation, and bleaching at ultraviolet (UV) wavelengths, resulting in net loss of color in particulates and net gain of largely UV-absorbing PDOM that also exhibited humic-type fluorescence. Solid phase proteinaceous material became less accessible to proteases after microbial decay, but regained this accessibility upon irradiation. Irradiation under anoxic conditions roughly halved production of PDOM, including chromophores and humic fluorophores. Oxygen enhancement of these reactions, along with production of peroxides, implies a strong role for photosensitization. Pigments, unsaturated lipids and tryptophan emerged as likely sources of reactive oxygen species. Lipid peroxides appeared as reactive intermediate products. If these reactions in the ocean scale to pigment loss as found in our experiments, at least 5-15% of particulate organic matter could undergo photodissolution before settling in some planktonic environments. This photodissolution would enhance remineralization by photic zone microbial communities and thus upper ocean elemental recycling.

Photodissolution converts particulate to dissolved organic matter, which may affect its availability to heterotrophic organisms. We examined the ability of planktonic microbes to utilize photodissolved organic matter (PDOM) obtained from irradiating coastal sediments and a preparation of algal membranes. About half of the organic carbon that was photodissolved from algal particulate detritus was subsequently available to microbes over two weeks of incubation in the dark, while that from the sediments appeared to be less bioavailable with utilization extents of 16-29%. Losses in total organic carbon during microbial incubation appeared as dissolved inorganic carbon, substantiating our inference of microbial usage. Accumulation of bacterial biomass was

small relative to respiratory loss, which may be due to low growth efficiency by bacteria or possibly grazing. Photoammonification converted some of the particulate nitrogen into inorganic ammonium; in the subsequent microbial processing of PDOM from sediments this ammonium was reincorporated into organic matter. Thus photodissolution shifts particulate organic matter to physical and chemical forms less available to metazoans and more available to osmotrophic microbes. This bioavailability on time scales of weeks indicates that PDOM produced in nearshore resuspension zones can add fuel to planktonic microbial regeneration processes while the water remains on the shelf, but that major fractions of the PDOM are likely to be exported offshore.

To better understand this bioavailability, we examined oxygen uptake during photodissolution. Over 18-24h irradiation periods, oxygen was consumed at a rate of about 0.28 mol per mol of particulate organic carbon that was photodissolved. We found dissolved inorganic carbon production as a result, but there was more oxygen consumption than DIC produced. This excess was small for sedimentary photodissolution, though greater than most similar experiments reported for terrestrial and coastal DOC photooxidation. The excess was considerably greater for algal detritus, and implies oxygen incorporation into organic matter – i.e. incomplete oxidation of the POC. We also found production of peroxides, consistent with earlier findings of conjugated dienes, and the possible creation of iron colloids resulting from iron photodissolution followed by reprecipitation at the neutral pH.

To provide an underpinning for the extrapolation of lab results to field reaction extents, we examined the optical properties of sediments from the Louisiana coastal zone. Using a light-integrating sphere attached to a spectrophotometer, several sediment samples were analyzed for absorption and scattering properties with and without chemical pretreatments to isolate chromophores. Both these chemical treatments and correlations with bulk composition (reducible iron oxyhydroxides and organic matter) point toward the reducible iron oxyhydroxides as dominant light absorbers in particles from this region; this finding is corroborated by second-derivative UV spectroscopy. Little of the particles' absorption at photochemically important wavelengths is due to organic chromophores. These iron chromophores appear to be partially lost in the transition from river to shelf, consistent with iron diagenesis in nearshore sediments.

This optical information was then incorporated into experiments targeting the apparent quantum yield (AQY) for the photodissolution reaction. We used a radiative transfer model to compute photon absorption by sediments in turbid suspensions from their measured optical properties. The photodissolution yields as a function of time and temperature were then normalized to this absorption. The reaction shows a strong temperature dependence, consistent with photosensitization. Photodissolution rates decrease with time over periods tens of hours long, but simple optical and physical models show that light exposures in the field may be an order of magnitude shorter, so 1- and 4-h irradiations were used to determine AQY's. Uniquely, the 1-h rates showed a positive dependence on reducible iron concentration, perhaps implicating photon absorption by iron oxyhydroxides as a stimulus for the reaction on these time scales. Nevertheless, the AQY's for sediment photodissolution are of similar magnitude as those found by other investigators for DOC photochemistry, suggesting that particulates can compete effectively with DOC for photons and subsequent photochemical reactions, especially in turbid areas where concentrations are similar.

These AQY's were then used in a remote sensing-based model to assess field reaction extents. MODIS satellite ocean color reflectance observations were processed via a new inversion algorithm to assess field concentrations and absorption coefficients of suspended sediments and chromophoric DOC. A depth-integrated model was developed to calculate photodissolution during 2007-2010 on an areal basis over the coastal region, and chromophoric DOC absorption, incident sunlight and temperature data were used to modulate the reaction. The MODIS reflectance-based model was compared with independent records of local wind speed and river discharge. A strong, non-linear relationship between the reaction and mean, daily wind speed was found, with the reaction proceeding slowly at speeds less than 4-6 m s⁻¹. The reaction is most significant in spring and summer though surprisingly independent of season, due to greater wind-driven sediment resuspension during seasons of lower solar irradiance. Integrated photodissolution rates contribute on the order of 1% of the DOC provided by combined Mississippi and Atchafalaya river inputs, but are likely of similar magnitude as photooxidation of DOC on an area-normalized basis.

This project provided funding for the PhD program of Ms. Margaret Estapa, who successfully defended her thesis in June, 2011 and will graduate in August of 2011.

Outreach activities for this project included participation in COSEE activities at the University of Maine, and a public outreach lecture at the University of Texas/Austin (Port Aransas) from which a web broadcast was made.