1999

Interactions on Minerals and Organic Materials Along the Salinity Gradient in Barataria Basin, Louisiana.

Jessica Anne Kastler

Louisiana State University and Agricultural & Mechanical College

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INTERACTIONS OF MINERALS AND ORGANIC MATERIALS
ALONG THE SALINITY GRADIENT IN BARATARIA BASIN, LOUISIANA

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Oceanography and Coastal Sciences

by

Jessica Anne Kastler
B.S., Louisiana State University, 1987
M.S., University of Virginia, 1993
May 1999
ACKNOWLEDGMENTS

I am amazed as I think back on it, how many people helped me with this work. It did not feel like I had such a well-developed network during some of my more frustrating moments. But I am very lucky to have friends and advisors, without whose help, I could not have completed this project. First, I thank the members of my committee. Dr. Gene Turner assumed I would do great things without nagging and introduced me to the papers from which I developed this project. He also supported this research financially, made interesting and increasingly meaningful comments on results throughout my progress, removed all prepositional phrases that introduced sentences in my writing, and became a friend. Dr. Ray Ferrell has aided me throughout both of my degrees at LSU. During my recent tenure, he welcomed me into his lab, opened interesting doors for my attention, and offered insight that has improved my understanding. He also provided access to the XRD and SEM Labs, where I got to know my husband and did some neat research. Dr. Bob Gambrell provided consultation about the different lab techniques I attempted; his care in reading the penultimate draft of this thesis detected several lapses of reasoning for me to correct. Dr. Jaye Cable put a lot of effort into reading my drafts, and frequently offered suggestions to help me with professional development. I also thank the representative of the Graduate School, Dr. Jim Robinson of the Chemistry Department for making me put my work into an unfamiliar context.

The faculty of the Department of Oceanography as a whole and as individuals has supported my efforts. I thank them for their interest and confidence, particularly Dr. Paul LaRock, who also helped me with SEM sample preparation and critical point
drying, and Dr. Sam Meyers who read a draft of one of my chapters. My work has been supported by a Louisiana State University Board of Regents Graduate Fellowship, The Ted Ford Memorial Award, The Joe Lipsey Memorial Award, and various assistantships I obtained through the Department of Oceanography and Coastal Sciences, and the Coastal Ecology Institute.

I thank Dr. Larry Mayer of the Darling Marine Center, University of Maine for providing prompt specific surface area analyses.

I thank Jim Lee and Tom Oswald for toting water and keeping up the Barataria Tradition. Charlie Milan, Gary Peterson and Erick Swenson also helped with field and lab efforts. Ms. Wanda LeBlanc was quite a trooper in my efforts in XRD and SEM imaging. Dr. Xiaogang Xie helped me a lot in the SEM lab. Dr. James Geaghan provided statistical consulting. Dr. Charles Sasser provided cooler space to store my water while the sediment settled; he also introduced me to the joy of marsh work long ago. For office, academic and technical support, I thank Pam Bloom, Craig Stevens and the assortment of undergraduate student workers passing through the DOCS office, particularly, Kelly, Bridget and Tammy.

I have really enjoyed life in Baton Rouge. For that I thank my family, particularly my Dad, Arthur Kastler; my sister, Marie Kastler; all of the Barrons; and our newest arrival, the noble canine Aimee. I have often found a nice escape from work in the community I found here with people like Naureen Qureshi, Mary and Terry Belou (and Katherine Gaye), Pati Delgado-Sanchez and Philippe Hensel (and poo-poot, Nicolas), the gardeners at Southside Community Garden, and my buddy Gene Wright. Friends from afar have lent me a hand at odd moments when they...
perceived that I needed it. With me despite distance since high school, thanks to Katherine Lynd and Bridget Scholnick. I am most grateful as well to Courtney Harris, Martha Sutula and Naureen Qureshi whose sporadic but confident email communications contributed to my unexpected sanity in the final stretches.

From our first meeting in the environmental chemistry of wetland soils, through our study dates in statistics and shared struggles with critical point drying, I have learned and laughed so much with my husband, Andrew Barron. I appreciate your staying awake with me, offering advice from your soil chemistry perspective, introducing me to your family, throwing yourself into gardening, learning to dance, teaching me to cook with chilis, letting me keep the dog... Thank you for all the fun, and everything else.
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ABSTRACT

Changes in the associations among mineral and organic materials in estuaries may control the nature and quantity of organic material (OM) preserved in sediment deposits or cycled in the water column. Estuarine sediment-OM attachments were examined using descriptive analyses and experiments to assess their response to salinity changes and the bioavailability of sedimentary OM. Desorption experiments compared the amount of organic carbon extracted from sediment in rinses of different salinity. Uptake experiments monitored changes in carbon and bacteria concentrations to compare the bioavailability of dissolved and sedimentary OM. Clay mineralogy, surface area and elemental analysis of suspended and deposited sediment were examined along the salinity gradient. Salinity, suspended sediment, dissolved and particulate organic carbon, and chlorophyll concentrations were used to describe water quality.

Experimental sediment OM releases of ~1-5% (deposit) up to 30% (suspension) were controlled primarily by sediment organic content and secondarily by salinity, pH and DOC. Bacteria consumed both DOM (~11%) and sedimentary OM (43-79%). The largest losses were from suspended sediment OM (65-79%), and corresponded to growth of the largest bacterial populations (30x10^6 cells mL^(-1)). Fine sediment was composed of smectite, illite, kaolinite and chlorite. Mineralogical variation was attributed to resuspension effects. Sediment surface area averaged 28.5 m^2 g^-1 (deposit) to 55.0 m^2 g^-1 (suspension). Deposited sediment averaged 4.1% organic carbon and 0.4% nitrogen; with values increasing upstream. Concentrations of both were higher in suspended sediment (OC = 8.3%, TN = 0.9%). Carbon to

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nitrogen ratios were lower in deposited than suspended sediment (~11.3 and 13.5, respectively), suggesting that suspended sediment was enriched in labile organic components. Physical characteristics, including clay mineralogy and surface area, control the amount of organic carbon attached to sediments. Environmental factors, such as distance from the mouth of the bay and chlorophyll concentration, determine the nitrogen content and thus the lability of attached organic material.

A conceptual model supported by the experimental results and descriptive data, suggests that labile OM adsorbs to sediment in productive regions and carries it to poorer regions where it can be released. Through this mechanism, suspended sediment influences the distribution and consumption of OM in estuaries.
CHAPTER 1
INTRODUCTION AND LITERATURE REVIEW

Interactions among minerals and organic materials modify the behavior of both constituents in an estuary. Sediment aggregation changes depositional patterns in estuaries by promoting settling of larger, faster settling particles in estuaries where fine sediments might not be likely to settle (Haven and Morales-Alamo, 1972; Schubel and Kana, 1972). Similarly, joining organic compounds to mineral grains affects the transport and transformation of organic materials. Marine aggregates concentrate organic substrate into a microhabitat where reactions take place at an increased rate over reactions occurring in the water column as a whole (Alldredge and Silver, 1988). Merely increasing the concentration of sediment in a reservoir can cause a shift from autotrophic to heterotrophic pathways when bacteria colonize clay aggregates in turbid water and limit light delivery to phytoplankton (Lind and Davalos, 1990). Organic material may also concentrate on sediment particles encouraging bacteria to attach to those particles and increasing their metabolic activity in the water (ZoBell, 1943). In sediment deposits on the continental shelf, preservation of the organic material that is deposited with sediment may depend on its association with mineral sediment grains. The positive linear relationship between sediment organic material and mineral surface area in continental shelf deposits has been attributed to preservation of the organic material by adsorption on the mineral surfaces (Mayer, 1994b).

Estuaries are sites where terrestrial freshwater mixes with marine saltwater. Along an estuarine gradient, both end-member sources supply different dissolved ions and detritus leading to numerous changes in water chemistry. The pH of estuarine waters generally increases from low values in freshwater to a basic pH of ~8 in marine
waters (Li et al., 1984), however a downstream pH decrease has been documented in blackwater estuaries (Beck et al., 1974). The gradient of the Tamar Estuary, U.K. illustrates the interactions of chemical and biological changes that occur along the salinity gradient. Oxygen and chlorophyll minima coincide with a peak in DOC, and many freshwater phytoplankton die in the vicinity (Morris et al., 1978).

Mineral and organic materials are introduced to an estuary from various sources. These materials may maintain associations that predate their entry to the estuary until the sediment is deposited in estuarine sediments or transported out of the estuary to the continental shelf. The attachments may instead disintegrate or change in the estuary, so that sediment organic material leaving the estuarine water column reflects a transformation from terrestrial to marine composition. The objective of this review is to summarize published information that pertains to the nature of mineral-organic associations and the role of these associations in determining the fate of both minerals and organic material in estuarine environments. The first sections describe the mineral and organic materials that are likely to be found in an estuary and how they are expected to behave when they are considered individually. Later sections describe organic sediment aggregates that are observed in natural environments and consider the mechanisms that link organic molecules to mineral surfaces. A discussion of the importance of mineral adsorption to organic material utilization is followed by description of some of the ways that mineral-organic attachments affect organic material cycling in natural environments. The importance of mineral attachments to organic material cycling in estuaries is discussed and followed by an introduction to the remaining chapters of this dissertation.
Mineral sediment in estuaries

The nature of mineral sediment in estuaries depends on the terrestrial and marine sources from which it is transported. The sediment is sorted during seaward transport, as denser and larger particles are dropped along the bed (Blatt et al., 1980). The size and composition of sediment depend on the source of sediment and the distance over which it has already traveled. Chemical weathering alters reactive igneous minerals during its transport from continental source areas. Much of the sediment traveling in suspension by the time the water reaches the estuary consists of fine sand or silt, and clay minerals.

Clay minerals in sediment are extremely fine-grained (< 2 µm effective diameter) particles that remain in suspension for long periods even in still water. Initial conceptions of clays as amorphous substances containing primarily particles similar to kaolinite changed to reflect the findings (Pauling, 1930) that different types of clay have specific structures and compositions (Grim, 1968). In general, clays are hydrous alumino-silicates composed of layers of adjoining tetrahedrons of silicon surrounded by oxygen and octahedrons of aluminum surrounded by hydroxide ions. The composition of a specific mineral is determined by the ratio of the types of layer in the unit cell (1:1 or 2:1, tetrahedral to octahedral sheets), and by substitution of various ions for the octahedral aluminum and tetrahedral silicon. Clays are chemically reactive because unit cells have charges that result from broken bonds at cell edges, ionic substitution within the lattice structure, and loss of the hydrogen atom on exposed hydroxyl groups. The charge on clay grains allows them to exchange ions in aqueous solution. Consequently, clays have been studied extensively for their role in
the storage of plant nutrients and toxins. The layer charge also contributes to the adsorption by clays of water and organic molecules. Through these mechanisms, layer charges control the plasticity and compaction of clays, and determine its behavior in suspension (Grim, 1968).

One of the processes that occurs in estuarine waters is flocculation of dissolved and fine particulate material. A charged particle in fluid accumulates ions of the opposite charge in a layer around it. Together, the layer of charge on the particle and the layer of counter-ions in the fluid are called the electrical double layer (van Olphen, 1977). If the repulsion between similarly charged particles is overcome, particles can approach each other closely enough for induced dipole, hydrogen or covalent bonds to join them. The addition of electrolytes compresses the electrical double layer of clay particles, allowing them to approach each other more closely and facilitating collisions that lead to flocculation (van Olphen, 1977). This phenomenon is well-documented in laboratory simulations (Bennett and Hulbert, 1986), but is not always observed under field conditions. Some researchers report no evidence of salinity flocculation (Eisma, 1986), while others have documented flocculation at different ranges of salinity, between 0 and 15 psu (Gibbs et al., 1989; Li et al., 1993; Syvitski, 1991). The observation that flocculation occurs where suspended sediment concentrations increase suggests any process that encourages collisions between particles contributes to flocculation (Kranck, 1981). Collisions caused by differences in particle settling rates and fluid shear can cause flocculation (Lick et al., 1993; Luettich et al., 1993). As is shown for dissolved inorganic ions such as Mn and Fe, the pH changes that

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occur along an estuarine gradient can also contribute to flocculation (Sholkovitz, 1976; Cai et al., 1998).

Packaging clay particles into larger flocs facilitates deposition and makes the estuary a sink for sediments (Mehta et al., 1989). Flocs contain sediment grains of all sizes and therefore cause the deposition of some fine grains that might otherwise not settle (Kranck, 1980). The turbidity maximum is an area where tidal current resuspension combines with estuarine circulation to generate a zone of locally high suspended sediment concentrations (Schubel, 1968). In particularly turbid estuaries (>20 g L⁻¹), settling sediment generates an ephemeral fluid mud deposit, which receives deposited sediment during slack tides and relinquishes them back to suspension when tidal velocity increases again (Gallane, 1974). The large concentration of flocculated sediments in the turbidity maximum suggests that flocculation may also contribute to the formation of turbidity maxima (Gibbs et al., 1989; Kranck, 1981).

Sediment flocs are widely described in estuarine environments. Those collected and observed microscopically are composed of unsorted grains, but the mode of the floc size distribution is proportional to the mode of the constituent grain size (Kranck, 1973). Flocs observed along the salinity gradient vary in size and composition as flocs break in the changing hydrodynamic conditions (Gibbs et al., 1989; Syvitski and Murray, 1981). This is supported by the observation in one location that estuarine floc size was a weighted average of the size of large freshwater flocs and smaller seawater flocs (Burban et al., 1989). The clay content of flocs influences their size and persistence in water; clay flocs were smaller but more
durable, while larger silt flocs were destroyed by turbulence and were not present at higher tidal current velocities (Li et al., 1993). The control of floc size and strength has been attributed to salinity, fluid shear, and suspended sediment concentration (Ani et al., 1991; Burban et al., 1989; Krone, 1978). Several researchers have documented bimodal size distributions of sediment flocs having different levels of structural complexity (Eisma and Kalf, 1986; Kranck, 1973; Krone, 1978). These distinctive distributions may be related to differences in the preservation potential of different-sized flocs. High suspended sediment concentration and fluid shear can cause collisions that lead to floc formation, and limit the size that flocs reach. Underwater photography is being used increasingly to observe flocs in the field and avoid the problems of breakage during sampling (Eisma et al., 1991).

The presence of flocs broadens grain size distributions of individual particles (Kranck, 1975), changes the settling behavior of sediment (Gibbs, 1985), and controls the microstructure of deposited sediments (Moon, 1972). Physical processes such as flocculation are not solely responsible for sediment aggregation (Schubel, 1969). Associations of organic material with sediment, for example in fecal pellets, are increasingly recognized contributors to aggregate formation. A complete understanding of sediment aggregation requires consideration of estuarine organic material.

Organic material in estuaries

Estuaries receive organic material from rivers, land or the coastal ocean, and produce it in situ through primary production. The quantity and quality of estuarine organic material varies seasonally with the discharge of terrestrial runoff to the estuary
(Zhang et al., 1992), and the occurrence of winter storms that resuspend sediment and bring marine material into the estuary (Reed, 1988). The introduction of suspended particulate material may be associated with increased particulate organic carbon (POC; Bianchi and Argyrou, 1997; Wolaver et al., 1986), or a proportional decrease of POC (Zhang et al., 1992). Tidal resuspension can increase the concentration of organic material in suspension (Wolaver et al., 1986). Other sources include groundwater advection, marsh seepage, surface runoff, and autochthonous production (Kemp and Boynton, 1984; Wolaver et al., 1986). Reported sinks of material include deposition with sediment, adsorption of dissolved OM to sediment grains, and biological uptake (Wolaver et al., 1986).

Organic material may be classified by size. Filtration commonly separates the particulate fraction from the dissolved fraction at 0.45 μm. Most bacteria are grouped with the particulate fraction, while viruses and smaller bacteria can pass through the pores (Christian, 1989). In recent years, ultrafiltration has been used to separate the colloidal size fraction that lies between the sizes of particulate and dissolved organic material. Colloids have high surface area relative to their volume, so they are chemically reactive and provide a link between the abundant dissolved organic component and the ecologically active, particulate component of estuarine organic material (Zsolnay, 1979). They may also be reactive because of their nutritional value (Sigleo et al., 1983). Both colloidal and particulate organic materials are composed of protein and carbohydrate matrices. Colloidal organic material from Chesapeake Bay has more oxygen containing groups and no terrestrially derived lignin, so it may be degraded more easily than particulate materials (Sigleo et al., 1982). Variations in
degradation could lead to functional differences between colloidal and particulate organic material.

A dominant functional component of dissolved organic material is humic material, which forms chemical bonds with pesticides and trace metals through chelation or adsorption (Fox, 1991). Although humic structures make up 40-90% of terrestrial organic material in an estuary (Fox, 1991) and have been studied extensively, they are not precisely defined chemicals. They are described as refractory, yellow to black, high molecular weight, alkali soluble polyelectrolytes. Humic acids are an organic matter subset that includes less soluble, higher molecular weight materials. Fulvic acids represent more soluble organic material that is lower in molecular weight (Thurman, 1985).

Terrestrial organic material has been shown to supply carbon and nutrients to the carbon cycle of estuaries (Naiman and Sibert, 1978). Isotope studies indicate that autochthonous dissolved and particulate organic materials are also cycled in the estuary (Simenstad and Wissman, 1985). The degradation or preservation potential of organic material varies with its source. Organic material transported from terrestrial soils arrives in the estuary already degraded. This organic material is thought to be resistant to marine degradation (Keil et al., 1997). Much of the organic material found in an estuary derives from terrestrial plant detritus, or from excretion and degradation products of aquatic organisms (Sigleo et al., 1982). Differences have been observed between freshwater and marine organic material such as relative depletion in nitrogen in freshwater humics (Hedges et al., 1992; Thurman, 1985). There is a greater relative contribution of aliphatic components in marine humics, while freshwater humics have...
more aromatic groups because the aromatic precursors, such as lignin, are typically found in land plants (Zsolnay, 1979). Colloidal organic material found in the water column is lower in aliphatic and aromatic characteristics than organic material in the deposit. It contains instead more labile constituents including carbohydrates and proteins that are rapidly recycled (Sigleo et al., 1983).

Like clay minerals and metals, organic humates can flocculate and settle from the water column before estuarine waters reach the coast (Beck et al., 1974; Hedges et al., 1992; Li et al., 1984; Zsolnay, 1979). In contrast, DOC often behaves conservatively in estuaries (Dai et al., 1995; Laane, 1980; Mantoura and Woodward, 1983), leading to conflicting interpretations about the behavior of organic material in estuaries. Some suggest that DOC behaves conservatively in parts of the estuary but flocculates in the low salinity zone (Morris et al., 1978).

In part, the confusion surrounding organic material behavior results from changes in the definition of DOC. Much of the work took place before widespread use of ultrafiltration to distinguish colloidal organic carbon. For example, Laane (1980) does not distinguish between colloidal and dissolved organic carbon, assuming that if mixing is faster than production or decomposition, organic material behaves conservatively. Separating the colloid fraction makes it possible to conclude that DOC is conservative while higher molecular weight organic molecules are susceptible to estuarine flocculation (Dai et al., 1995; Mantoura and Woodward, 1983; Sholkovitz et al., 1978).
Mineral-organic interactions

Aggregation

Studies that have examined either mineral or organic materials in aquatic systems repeatedly report that neither aspect can be considered alone and still give a complete picture of the processes taking place in the environment. Associations between them link the fates of both components in estuaries. The physical changes that occur along the salinity gradient can cause flocculation of both mineral and organic material acting independently. Sediment in natural waters is coated with a thin film of organic material (Cosovic and Vojvodic, 1989; Hunter and Liss, 1979), that makes it slower to flocculate upon encountering seawater than sediment that is free of organic material, such as that used in laboratory simulations (Gibbs, 1983).

Mineral and organic material aggregation involves both physical and biological processes. This aggregation may result in larger suspended particles that may or may not be related to changing salinity. In terrestrial soils organic ions are assumed to cause clay dispersion that leads to decreases in hydraulic conductivity. Changed hydraulic conductivity may occur as a result of two processes: 1) organic coatings on the mineral particle increase surface roughness, thereby decreasing van der Waals attraction (Heil and Sposito, 1995); or 2) organic materials enhance surface charges such that greater salt concentrations are required to flocculate clay particles (Frenkel et al., 1992). Studies conducted in aquatic systems increasingly recognize that organic materials promote aggregation of mineral particles. Some authors assume a high degree of biological control, for example, aggregate formation by invertebrate fecal pellet production and attachment of mineral flakes with microbial film coatings (Paerl
and Shimp, 1973; Zabawa, 1978). Others maintain that physical processes acting alone are sufficient to form sediment aggregates (Kranck and Milligan, 1980). The importance of organic materials as a binder that strengthens sediment aggregates is readily acknowledged (Bennett et al., 1991; Syvitski, 1991). Invertebrates play a major role in aggregate formation by binding sediment in fecal pellets that are small and durable (Schubel and Kana, 1972). Small aggregates may collide and form macroflocs (Eisma and Kalf, 1986). Floc size is related to organic material binding strength, so that different organic materials will make different sized flocs (Eisma and Kalf, 1986).

The influences of salt, current speed and organic material availability control the appearance of mineral organic aggregates. Aggregate size is not necessarily related to suspended sediment concentration or tidal velocity (Wells and Shanks, 1987). Particles suspended in deep water of the Wadden Sea were coarser and higher in organic content that those of shallow waters, because shallow water aggregates were regularly deposited and resuspended (Eisma and Kalf, 1986). The hypothesis that salt flocculation promotes estuarine aggregation had been discarded by some because salt may actually reduce aggregate strength by mobilizing polysaccharide binders (Eisma, 1986). Nevertheless, variation is observed among aggregates collected along the estuarine gradient. Some researchers report that mineral grains, which are transported individually in river water, flocculate downstream and become incorporated into increasingly complex aggregates as marine organic material becomes available for support (Pierce, 1991; Syvitski, 1991). In contrast, aggregates in the nutrient enriched freshwater reaches of Barataria Basin were larger and more
numerous than the small branched aggregates observed in saline waters (Chapter 4). Although the freshwater aggregates incorporated many biogenic particles, the only organic material in saltwater flocs were mucous strands that bound clay flakes. These disparate observations indicate that aggregates vary according to local environmental conditions.

**Attachments**

*Attachments between mineral grains and organic material may be mediated by the nature of the surfaces involved, or they may be determined by the character of the solution in which the interaction occurs, such as hydrophobic expulsion (Westall, 1987).* Surface-mediated attachments include electrochemical interactions like hydrolysis, complexation, ligand exchange, hydrogen bonding and polar attractions (Westall, 1987). Mineral composition exerts some control on the type of attachment between sediment and organic molecules. Oxides of aluminum and iron attach to organic materials through ligand exchange (Baccini et al., 1982; Tipping and Cooke, 1982), while attachments between aluminosilicate minerals and organic molecules are often attributed to hydrophobic expulsion by the solution (Hedges, 1977; Taylor et al., 1994b; Zutic and Tomaic, 1988). The mineral substrate may also influence the composition of the attached organic molecule. Calcium carbonates select different organic molecules from those chosen by silica (Carter, 1978). Within the range of composition of clay minerals, kaolinite prefers more acidic amino acids while montmorillonite prefers more basic ones (Hedges and Hare, 1987). Preferential selection of certain organic molecules by a mineral grain result from electrostatic differences, functional group reactivity, repulsion between different adsorbed
mechanisms and steric arrangements of molecules (Gu et al., 1995; Hedges, 1977; Hedges and Hare, 1987; Tipping, 1981; Zutic and Tomaic, 1988).

Hydrophobic attraction is the most important process in establishing the initial coating on particles (Zutic and Tomaic, 1988). In the estuary this mechanism is consistent with observations that more organic material adsorbs onto sediment in higher salinity waters (Kirchman et al., 1989). High ionic strengths in saltwater encourage the repulsion of organic molecules, isolating them with mineral particulate material so that the organic and mineral surfaces are likely to adhere. However freshwater has lower pH to maximize the adsorption of organic molecules to sediment grains (Zutic and Tomaic, 1988). Fractionation of the aqueous organic phase may occur (Gu et al., 1995) because the most hydrophobic groups are adsorbed to mineral grains first (Cosovic and Vojvodic, 1989; Gu et al., 1995).

Observations about the effect of underlying mineral composition are drawn from lab experimentation using organic free mineral surfaces. The binding sites of natural mineral surfaces are almost completely occupied by an organic coating (Baccini et al., 1982). Once established, the organic film dominates the surface chemistry of mineral-organic particles. Charge and composition of underlying minerals become unimportant (Cosovic and Vojvodic, 1989; Hunter, 1980; Hunter and Liss, 1979; Taylor et al., 1994b). The amount of organic material already attached to mineral grains is directly related to adsorption of other organic molecules such as hydrophobic pollutants (Karickhoff et al., 1979). This illustrates how chelation binds organic material to mineral grains using an organic link (Stevenson and Ardakani, 1972).
The organic coating on mineral grains can be a complete or incomplete monolayer, or it can be thicker than a monolayer (Baccini et al., 1982). Protein films may be established in a thin layer, or outer layers may be degraded or desorbed leaving only a thin layer (Taylor et al., 1994a). Strong hysteresis has been documented between the processes of adsorption and desorption (Gu et al., 1995), however protein adsorption to particles is reversible except when the concentration of protein in the solution is low (Kirchman et al., 1989). Outer layers of protein desorb more rapidly than those that are bound to the metal substrate surfaces (Taylor et al., 1994a).

Natural sediment textures influence the amount and composition of organic material held by sediment. An established relationship between sediment grain size and organic content is attributed to a single layer of organic molecules binding to the capacity of the mineral surface area (Mayer, 1994b; Suess, 1980). The monolayer coverage for aluminosilicate minerals is ~0.8 mg OC m\(^{-2}\) of sediment surface area (Mayer, 1994b). Some broad differences in composition of organic material on sediment of different sizes arise because of differences in sources. In the Columbia River estuary, sand-sized particles are associated with vascular plant detritus while clay grains are more likely to originate in soils and include nitrogen rich soil organic material (Hedges et al., 1994; Keil et al., 1994a). Sediment organic contents lower than the expected monolayer equivalent level (0.8 mg OC m\(^{-2}\)) have been observed in deltas, and in the fine fraction of estuarine and continental shelf sediments (Keil et al., 1994b; Mayer, 1994b; Chapter 4). Mayer (1994a; 1994b) suggested that unfilled attachment sites on mineral grains in deltaic regions could occur either because
sediment delivery to deltas is very high, or because the sediment originates in deep soils below the organic-rich A horizon. These suggestions are inconsistent with widespread agreement that virtually all mineral grains are covered with organic material in natural waters (Hunter and Liss, 1979).

The fine grains that characterize this sediment are dominated by smectite, which has higher surface area than other clays. A surface area measurement is not expected to include the surface area that does not act as binding sites for organic material adsorption (Mayer, 1994b). However, surface area measurements in sediment containing smectite may include some of the unavailable interlamellar area of the expandable clay (Keil et al., 1994b). Acknowledging this possibility suggests that smectite and other expanding clays do not play a special role in organic carbon preservation in sediments (Mayer, 1994b). Strong relationships between organic carbon and smectite content of sediment indicate that although interlamellar surfaces are not used for adsorption, the increased external surface area of smectite controls sediment organic content (Keil et al., 1994b; Chapter 4). The decline in organic loading of sediment that has high surface area is most notable in suspended estuarine sediment (Chapter 4). Sediment that remains in suspension is particularly fine and particularly rich in smectite, suggesting that increases in surface area are accompanied by an increase in surface area that is unavailable for organic attachment.

**Utilization of attached organic material**

Large bacterial populations on marine snow aggregates undergo rapid succession because of rapid rates of photosynthesis, decomposition and nutrient mineralization (Alldredge and Silver, 1988). Estuarine aggregates also provide sites
for active bacterial feeding (Alber, 1997; Plummer et al., 1987; Zutic and Tomaic, 1988). Several laboratory studies have considered bacterial use of various types of organic material adsorbed to different substrates. An early study established that adsorption to glass can concentrate nutrients, making it more likely that bacteria would be able to use them (ZoBell, 1943). Adsorption of protein to glass at low concentrations facilitated bacterial use of the protein whether by concentrating it on a surface, or by causing proteins to unfold and expose more bonds for hydrolysis (Taylor, 1995). However, adsorption reduced bacterial degradation of adsorbed proteins in a similar study (Nagata and Kirchman, 1996). Bacterial consumption may depend on the amount of organic material adsorbed to the glass surface. High concentrations of proteins adsorbed to glass can be used quickly because more organic material is available on the glass surface (Samuelsson and Kirchman, 1990). These observations of model organic molecules on glass show no dependence on substrate composition. When clay minerals are used as substrate, the consumption of model organic molecules show differences that are attributed to their attachment to different clay minerals (Dashman and Stotzky, 1986). Experiments that used natural organic material and water column bacteria show that organic material that can be removed from sediment grains is susceptible to degradation by water column consumers (Keil et al., 1994a; Chapter 3). Large aggregates containing organic material that is recently produced by phytoplankton are used quickly (Alldredge and Gotschalk, 1990). Sinking particles, resuspended particles and those that are collected from deep water are similarly less attractive to bacterial consumers (Alber, 1997; Paerl, 1973; Plummer et al., 1987). Estuarine consumers use higher proportions of organic material bound to
suspended sediment than deposited sediment (Chapter 3). Nevertheless, sedimentary organic material is a substrate that bacteria will consume, whether it is in the water column or the deposit. The organic material that is ultimately deposited with sediment may show evidence of selective degradation.

**Mineral-organic interactions in OM cycling in natural environments**

**OM transport, deposition and preservation in sediment**

Aside from changing trophic relationships, and mineral and contaminant transport patterns, mineral-organic interactions influence long-term carbon cycling and preservation in sedimentary deposits. Organic material is deposited with sediments in terrestrial, coastal and marine environments. Rivers are assumed to carry a large supply of terrestrial organic material to the ocean, where it may make up a large part of ocean DOM because of its refractory nature (Mantoura and Woodward, 1983). This recalcitrant organic material must be remineralized in the ocean because labile plankton make up the bulk of marine DOM (Hedges et al., 1992). In the deep ocean, clay and carbon deposition are linked; both settle to the sea floor as organic aggregates during pulses of biological activity (Fischer, 1991). Some organic material is delivered to sediments in the Gulf of Mexico by lateral transport through bottom waters across the shelf to the continental slope (Bianchi and Argyrou, 1997; Hedges and Parker, 1976). There is also considerable deposition of autochthonous carbon as fecal pellets settle in the Gulf (Qureshi, 1995). Detection of terrestrial organic material indicators in some sediments argues against extensive degradation of terrestrial organic material (Hedges and Parker, 1976), but sediments in other coastal
locations show variation in the preservation of terrestrial carbon and nitrogen (Mayer et al., 1988).

Most organic material found in sediment deposits is attached to mineral sediment grains (Keil and Hedges, 1993; Mayer, 1993). By comparing reaction times of organic material from marine and terrestrial sources, Hedges (1992) concluded that grains would preferentially sequester terrestrial organic material, however less than 20% of terrestrial organic material is preserved in marine soils. Keil et al. (1994) found no relationship between primary production and the amount of sedimentary organic carbon preserved in Washington coastal sediments, and attributed the primary control of sediment organic content to surface area relationship. However primary production has been associated with covariation between sediment and organic material (Grimalt and Albaiges, 1990), and enrichment has been observed in near surface sediments where organic material delivery is high (Mayer, 1994b). With depth in a given core, organic material levels fall to a refractory background level of material that is adsorbed to mineral surfaces and protected from degradation by its placement within micropores.

Autochthonous organic material is degraded while it travels to the seafloor (Fisher et al., 1979; Wakeham and Ertel, 1988). A fraction of the initial organic material survives destruction during sinking and sedimentation, but its functional characteristics may change (Meyers, 1994). After sedimentation, between 30% and 90% of deposited organic material is remineralized by sedimentary organisms during early diagenetic processes (Henrichs, 1992). The rate of consumption depends on rate of delivery of both sediment and organic material to the deposit, and may depend on
whether dissolved oxygen levels allow oxic degradation reactions to proceed (Canfield, 1994; Henrichs and Reeburgh, 1987). Early diagenesis includes degradation of organic material, but occurs coincidentally with the production of new species that also change the character of the organic material preserved in the deposit (Macko et al., 1994).

**Sedimentary organic material cycling in estuaries**

These studies show that mineral associations control how much sedimentary organic material is deposited, how much is preserved, and how it is transported. These questions are particularly important in the estuary because estuaries are the source of much of the terrestrial organic material that enters the ocean. But the transport of organic material through the estuary remains unclear (Lee and Wakeham, 1992). With conflicting reports about the conservative behavior of organic molecules in an estuary, it is difficult to predict concretely whether OM will be transported through the estuary, deposited in estuarine sediment, or undergo transformations that result in the transport or deposition of a different type of organic molecules. The uncertainty about associations between mineral and organic materials complicates this issue further. Only strong adsorption can prevent loss of organic molecules from sediment by diffusion (Henrichs, 1995). Therefore, freshwater organic material adsorbed to sediment should be replaced by organic material from marine sources as marine organic material begins to dominate DOC during the transport of sediment through estuaries. The results of isotopic analysis of colloidal organic material in different North American estuaries shows that such a transformation from terrestrial to estuarine organic material can occur (Guo and Santschi, 1997). If a transformation
also occurs in mineral-attached organic material, it could explain the destruction of freshwater organic material on sediment in the estuary and the paucity of terrestrial organic material on sediment in marine deposits (Hedges et al., 1992; Hedges et al., 1997).

The microbial consumption of experimentally released sedimentary organic material indicates that these compounds are labile when they are not attached to mineral grains (Keil et al., 1994a; Chapter 3). High rates of bacteria production and hydrolytic enzyme activity on suspended sediment aggregates suggest that at least some of the organic material is also consumed while it is being transported in suspension (Alber, 1997; Plummer et al., 1987). Berger et al. (1984) reported no evidence for a systematic change in the exchangeable organic material on sediment collected along an estuarine gradient. However, several lines of evidence suggest that organic material exchanges between suspended sediment grains and water as a function of the concentrations of organic material on sediment and in the water. The amount of organic material released from sediment in water varies with water quality, including changes in DOC concentration (Chapter 2). In addition, the partition coefficients of hydrophobic pollutants on sediment depend on organic content of the sediment (Karickhoff et al., 1979). Perhaps organic material is bound to mineral grains in multiple layers, and the outer layers may become available to consumers by detachment from the mineral grain.

Like organic material that is not associated with mineral grains, sedimentary organic material may be used close to the location where it is produced or enters the estuary (Tan and Strain, 1983). It may instead be transported with flowing water for
use elsewhere or transported out of the estuary like dissolved organic material in other
locations (Biggs and Flemer, 1972; Guo and Santschi, 1997). As sediment moves
downstream, attached organic material is consumed or exchanges from mineral
surfaces, contributing to compositional variations in sedimentary organic material
observed along the gradient (Chapter 4). In this way labile organic material is
depleted of sedimentary organic material, and like the refractory components of
unattached organic material, is transported away from the source (Grimalt and
Albaiges, 1990). Although depleted of labile components with respect to sedimentary
organic material found upstream, the sedimentary organic material transported
downstream is more labile than unattached organic material downstream (Chapter 3).
As a result, sedimentary organic material provides a reservoir of organic material
beyond what is available as dissolved organic carbon.

Vertical gradients in the attachment and transport of sedimentary organic
material also contribute to the sedimentary organic material cycling in estuaries.
Microbial activity on suspended sediment aggregates varies in marine systems with
the type and depth of the aggregate (Alldredge and Gotschalk, 1990; Wakeham and
Ertel, 1988). Similarly, estuarine aggregates found near the surface have different
compositions and are more heavily utilized by microbes than particles in near bottom
suspensions (Alber, 1997; Morris et al., 1987; Plummer et al., 1987). These
observations suggest that sediment organic material is removed or transformed during
settling of the mineral particles.

Some sedimentary organic material may be deposited in estuarine sediments,
because the oxygen required to respire organic material is often unavailable in the
water column or sediments (Gambrell and Patrick, 1978; Kemp, 1989). More organic material could be preserved than is present in the monolayer coverage if the amount adsorbed to sediment reaches equilibrium with dissolved organic material rich pore water (Hedges and Keil, 1995). Sediment in the deposit is depleted of organic material, particularly the labile components (Sigleo et al., 1983; Chapter 4). This may result from stimulated remineralization of organic material by oscillatory conditions of redox that can occur in estuarine sediments (Aller, 1994; Aller et al., 1996).

The transport of nutrients from the deposit back to the water column suggests that deposited sediment acts as an important source for water column production during some seasons (Boynton et al., 1980; Nixon, 1982; Zeitzschel, 1980). Resuspension may reintroduce particulate organic material from the estuarine bed into suspension (Wainright, 1990; Wolaver et al., 1986). Upon resuspension there is consensus that organic material is further depleted prior to its return to the bed (Oviatt and Nixon, 1975; Walsh, 1992). Repeated cycles of suspension and deposition have been called ‘rebound’ in marine sediments and contribute to the depletion of organic material storage in deposited sediments (Walsh, 1992). Desorption experiments show that sediment organic material releases result from changes in organic carbon concentrations in water and imply that the exchange is reversible (Chapter 2). Organic material will adsorb onto sediment surfaces if the DOC concentration is high enough. Consequently, the effect of resuspension to deplete or enrich the sediment organic content may depend on how high the sediment is resuspended in the water column and how long it remains there to take accumulate organic compounds. The storage potential of estuarine sediments may change with hydrodynamic conditions.
along the gradient. An increased tendency of wave or tidal action to resuspend sediment downstream results in reduced storage of organic material in sediments (Oviatt and Nixon, 1975).

Estuarine transport of organic material with sediment may follow the model proposed by Kemp and Boynton (1984) of undergoing repeated cycles of deposition and resuspension as it moves downstream in the estuary. This process can remove much of the attached organic material from sediment before it leaves the estuary. Mineral-attached organic material can be significant in organic material cycling within the estuary through the exchanges of organic material to the water and the persistent enrichment of sedimentary organic material relative to unattached dissolved organic material.

Summary of dissertation components

This dissertation includes experimental and descriptive studies that were undertaken to elucidate mineral and organic material associations in estuaries. Results of my studies have been incorporated into the preceding literature review to provide context for my work, and to show how it fits into the body of literature on mineral-organic interactions. Each study is introduced below to show its contribution and the approach with which it address the basic question of mineral and organic material associations in estuaries.

Chapter Two addresses the actual attachments of organic material to sediment surfaces in an estuarine environment. This study was developed to address the question posed by Lee (1994b) and Henrichs (1995) about whether salinity changes in estuaries encourage removal and replacement of terrestrial organic material attached to

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mineral grains. Desorption experiments indicated that organic material exchanges between mineral surfaces and water depend on the organic content of sediment. Water quality changes including organic carbon concentration, pH and salinity also play a role. A conceptual model developed from these results proposes that organic material continually exchanges between mineral grains and surrounding water to maintain a balance of organic material on the surface and in estuarine water (Fig. 1.1).

Figure 1.1. Conceptual model of organic material exchanges between sediment particles and surrounding water. Plus symbols indicated ions in salt water. Straight thick arrows indicate organic material adsorption to sediment; curved thin arrows indicate desorption from sediment. Organic exchanges occur in both directions between sediment (parallelograms) and the water at all points. Bacteria (open-mouthed profile) eat more labile organic material (closed circles) before eating less labile organic material (open circles).
Chapter Three is concerned with the significance of organic material exchanges in estuarine carbon cycling, and the lability of sedimentary organic material. Experiments removed organic material from suspended and deposited mineral grains and inoculated it with estuarine bacteria. The lability of dissolved organic material, which has been documented elsewhere (Kroer, 1993), was examined for comparison. All forms of organic material were consumed and incorporated into bacterial biomass, but higher percentages of sedimentary organic material were used, particularly organic material removed from suspended sediment (Fig. 1.1). The increased lability of sedimentary organic material suggests that attachment to sediment grains offers some protection from degradation to labile organic molecules.

Chapter Four examines variation in organic characteristics of suspended and deposited sediment collected in Barataria Bay, Louisiana. Suspended sediment includes more organic material, which is generally lower in C:N ratio than organic material attached to deposited sediment. The dominant constituent of organic material is organic carbon. The organic carbon content of suspended sediment is strongly related to surface area and the abundance of the clay mineral smectite. The nitrogen content, which contributes to the bioavailability of organic material, is related to mineral surface area and the chlorophyll \( a \) concentration in the water. Thus, the amount of organic material adsorbed to sediment is determined by its physical characteristics, while the biological use of the adsorbed organic material depends on environmental factors. Chapter Four also examines suspended sediment aggregates, and describes how the observed sediment and aggregate characteristics fit the model of sediment-water exchanges of organic material.
The results of these three chapters provide a consistent picture of how sediment interacts with organic material in the estuary. Exchangeable attachment to sediment provides a mechanism of organic material transport through the estuary, a temporary reservoir of labile material in suspension, and through deposition, a storage facility for degraded organic material.
CHAPTER 2
EXCHANGES OF ORGANIC MATERIAL BETWEEN SEDIMENT AND WATER ALONG AN ESTUARINE SALINITY GRADIENT

Introduction

Associations between mineral grains and organic material (OM) change the behavior of both constituents in natural environments. Organic molecules can form the bridge between clay domains to make large aggregates (Bennett et al., 1991), or change the transport potential of clay sediments (Dade et al., 1991). The attachment of organic molecules alters surface properties (Hunter and Liss, 1979), leading to changes in sediment affinity for trace pollutants (Davis et al., 1980). These factors may influence patterns of sediment deposition in estuaries (Preston and Riley, 1982).

Attachment to mineral grains also influence the fate of organic molecules. Organic material adsorbed to settling particles can be transferred to anaerobic or colder environments where degradation occurs at a different rate. Suspended mineral grains also provide a substrate that concentrates nutrients (ZoBell, 1943), so adsorption may enhance bacterial growth and reproduction (Taylor, 1995). However, it is questionable whether bacteria can use adsorbed OM (Dashman and Stotzky, 1986). Adsorption to mineral grains may even protect labile OM (Keil et al., 1994a; Mayer, 1994b). Henrichs (1995) discussed the possibility that selective desorption along a salinity gradient encourages exchanges of terrestrial OM for marine OM on mineral grains.

Suspended aggregates formed by mineral-organic attachments are highly reactive sites of bacterial feeding in estuaries (Zutic and Tomaic, 1988). The reactivity of the aggregates may depend on their settling behavior. Particles that
remain suspended throughout their transport in the estuary not only have higher
organic carbon (OC) and pigment concentrations than resuspended sediment, but also
show higher bacterial production and hydrolytic enzyme activity (Alber et al., 1995;
Plummer et al., 1987). These studies corroborate work showing enhanced biological
activity on marine aggregates (Alldredge and Silver, 1988).

The interactions between an organic molecule and a mineral grain are
electrochemical, including hydrophobic attraction, van der Waals attraction, ligand
exchange and hydrogen bonding (Westall, 1987). Sediment composition influences
the mechanism of attachment. Early attention to aluminum oxides established the
occurrence of ligand exchange in adsorption of organic material (Baccini et al., 1982;
Tipping, 1981). In systems dominated by aluminosilicate minerals, hydrophobic
attractions are more often cited as the bonding mechanism (Hedges, 1977; Zutic and
Tomaic, 1988). Selectivity in the attachment has been attributed to functional group
reactivity, repulsion among adsorbed groups, and steric arrangements (Hedges, 1977;

Many studies assume desorption is parallel and opposite to the process of
adsorption. A pronounced hysteresis between adsorption and desorption isotherms
indicates that desorption cannot be understood as the reverse of adsorption (Gu et al.,
1995). Adsorption studies suggest hydrophobic interactions control attachments of
aluminosilicate minerals, however the removal of OM has not received the same
amount of attention.

The objectives of this work were to examine the desorption phenomena of
natural organic solutes from mineral sorbates, and determine whether salinity controls
OM exchange on mineral grains. The results were used to examine the influence of sedimentary OM on water column cycling and preservation potential of OC in the estuary.

Methods

Field site and collection

Barataria Bay is a shallow (mean depth, 2 m), well-mixed estuary west of the Mississippi River (Fig. 2.1). Sediments are dominated by silt and clay that enter the estuary from drainage of forests and agricultural fields or from the Gulf of Mexico during frontal passages. Deposited sediment may also be resuspended and recycled within the estuary.

Surface water (500 mL) was collected monthly in 1994-1996 along a transect from the Gulf of Mexico to Lac des Allemands. Single, larger volume (160L) surface water samples and bottom sediment were collected at selected stations (Fig. 2.1) on different dates. An Eckman dredge was used to sample bottom sediment. Approximately 250 mL of sediment were subsampled, placed on ice, and refrigerated until analyzed. The water samples were collected with a bucket and refrigerated in the laboratory. Sediment was concentrated by settling for 24 h, after which overlying water was siphoned off. The remaining sample was centrifuged to separate the sediment for use in the desorption experiment.

Characterization

Salinity was estimated in the field with a refractometer, then verified using a conductivity meter. Filtered water samples (Whatman GF/F, mesh diameter 0.7 μm) were analyzed for dissolved organic carbon (DOC) on a Shimadzu TOC5000A using
platinum catalyzed oxidation at 670°C. Total suspended sediment was determined by drying rinsed, filtered samples (Whatman GF/C, mesh diameter 1.2 μm) at 60°C for 24 h.

Figure 2.1. Map of Barataria Basin, Louisiana showing sample collection locations. Numbers of collection stations correspond to stations along a transect from the Gulf of Mexico to Lac des Allemands. For sampling dates and water quality information see Table 1.

Small amounts of suspended and deposited sediment were dried at 60°C and ground. Organic material content (SOM) was estimated as the percent weight loss of
dry sediment after ashing at 550°C. Specific surface area (SSA) was determined on hydrogen peroxide-treated sediment using the one-point BET (Brunauer-Emmett-Teller) method and the N₂ adsorption isotherm (Mayer, 1994b).

The fraction of sediment that consisted of OM not associated with mineral grains was found by agitating subsamples in saturated cesium chloride (density = 1.9 g cm⁻³). Subsequent centrifugation separated mineral grains from less dense OM (Prahl and Carpenter, 1983). Particulate OM accounted for less than 3% by weight of the samples used here; large organic particles were removed from samples before the experiment.

Experiment

Synthetic seawater rinses of varying salinity (0, 2, 4, 16 psu) were used to estimate exchangeable organic carbon (EOC) associated with suspended and deposited sediment collected from the five stations shown in Fig. 2.1. Distilled water was used for the 0 psu rinse. Other rinse waters were made using distilled water and appropriate weights of synthetic seawater solids (Instant Ocean). Aliquots of sediment were added to pre-weighed, 50 mL centrifuge tubes, and weighed to determine their wet weight (~0.2 g). Duplicate tubes were prepared for suspended and deposited sediment collected at each station for each of the four different treatment salinities. Each centrifuge vial was filled to a level of ~20 mL with rinse water and sediment dispersed. Vials were shaken for ~12 h, after which samples were centrifuged for 30 minutes at 3000 rpm, and the supernatant siphoned and analyzed for OC using the Shimadzu TOC analyzer. Blank samples of different rinse treatments were also analyzed and the OC values obtained were subtracted from corresponding samples to
adjust for the carbon contribution from the synthetic seawater. New rinse water was added to each sample and the rinsing process repeated five times. The sediment was dried and weighed after the rinses were completed. The exchangeable organic carbon (EOC) was expressed as mg carbon removed per g of sediment.

Cumulative totals of EOC were analyzed to determine significant statistical differences using a two by two by four factorial analysis of variance in SAS Version 6.12 for Windows (SAS Institute, 1996). Main effects were location (station 7, 30), environment from which sample was collected (suspension, deposit) and the four different rinse salinities (0, 2, 4, 16 psu). This analysis included data from stations 7 and 30, which were obtained as described above.

The basic experimental procedure was modified for several of the samples. The December sample (station 12) was agitated in five rinses at the same salinities, but each rinse lasted one hour. The August samples (stations 4, 21) were agitated in rinses of 0 and 16 psu salinity for 20 consecutive 12 h rinses, to examine the effect of continuing treatments.

Organic Carbon: Nitrogen (C:N) ratios were determined on sediment from stations 7, 12, and 30 using both untreated samples and samples that had been used in the experiment. Sediment was dried, weighed and ground, and inorganic carbon was removed with dilute hydrochloric acid. Carbon (SOC) and nitrogen were measured using a Perkin Elmer CHNS/O analyzer model 2400. Sedimentary organic carbon was estimated for sediments from stations 4 and 21 using the empirical relationship between SOC and SOM obtained for sediments from stations 7, 12, and 30. The
percentage of SOC removed in the experiment was calculated using original SOC and EOC.

Results

Sediment and water characterization

The three-year average of monthly salinity measurements showed a gradual decrease from about 20 psu at the mouth of Barataria Bay to the freshwater regions (Fig. 2.2a, Table 2.1). Salinity measured at stations 12, 21, and 30 on the days when large water samples and bottom sediment were collected were within the annual range of averages for each station. However, station 7 was sampled when the measured salinity was below average because of recent rainfall. Station 4 water was more saline than average because of southerly winds bringing Gulf water into the estuary.

Suspended solids concentrations varied little from saline to fresh water, with a range of 20 to 40 mg L⁻¹ along the transect (Fig. 2.2b). Most stations had lower than average suspended solids concentrations because of calm weather on days when large samples were collected. Station 12 water samples were turbid (145 mg L⁻¹) because of resuspension during a thunderstorm.

The organic content (SOM) of suspended sediment generally increases from low values in saline water (~25 mg/100 mg) to values approaching 50 mg/100 mg in freshwater Lac des Allemands (Fig. 2.2c). The organic content of suspended sediment collected for the experiments was near average values. Although there is also a general trend to increase water column DOC in freshwater, there is not a strong relationship between suspended sediment organic content and DOC. However, the SOM of deposited sediment followed DOC closely (Fig. 2.3). There was no strong
relationship between organic contents of suspended and deposited sediment. Water quality and sediment characteristics from all five stations sampled for both experiments are summarized in Table 2.1.

```
<table>
<thead>
<tr>
<th>Station</th>
<th>a) Salinity (psu)</th>
<th>b) TSS (mg L⁻¹)</th>
<th>c) SOM (mg (100mg sediment)⁻¹)</th>
<th>d) C:N</th>
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Figure 2.2. Water and sediment characteristics averaged from monthly data collected along a transect (solid lines with standard error), and corresponding values on collection dates for the samples used in this study (plot symbols). Each point corresponds to the station whose number is above it. a) Salinity in psu; b) Total suspended solids in mg L⁻¹. c) Percent organic content (SOM) of suspended sediment (line and up-triangles) and deposited sediment (down-triangles), and dissolved organic carbon concentration in water in mg L⁻¹ (circles). d) Organic carbon to nitrogen ratio for stations 7, 12, and 30, deposited sediment (squares) and suspended sediment (circles); the error bars indicate standard error of 5 measurements on untreated sediment and sediment treated in each of 4 saline rinses.
Table 2.1. Summary of sediment and water quality characteristics and experimental results. Station number corresponds to location on map in Figure 1. Environment S indicates suspended sediment, D is deposited sediment. Experimental results after 20 rinses are given in parentheses next to 5-rinse results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water Quality</th>
<th>Sediment Characteristics</th>
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<tbody>
<tr>
<td></td>
<td>DOC mg L⁻¹</td>
<td>Salinity ppt</td>
</tr>
<tr>
<td>Station</td>
<td>Date sampled</td>
<td>mg L⁻¹</td>
</tr>
<tr>
<td>4</td>
<td>Aug-97</td>
<td>3.6</td>
</tr>
<tr>
<td>S</td>
<td>Dec-96</td>
<td>9.3</td>
</tr>
<tr>
<td>D</td>
<td>May-97</td>
<td>11.7</td>
</tr>
<tr>
<td>21</td>
<td>Aug-97</td>
<td>14.4</td>
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<tr>
<td>S</td>
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<td>5.8</td>
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<tr>
<td>D</td>
<td>May-97</td>
<td>11.7</td>
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<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental Results</th>
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<tbody>
<tr>
<td></td>
<td>EOC (mg g⁻¹ sediment)</td>
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<tr>
<td></td>
<td>0 ppt</td>
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<tr>
<td>Station</td>
<td>Date sampled</td>
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<td>Aug-97</td>
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<td>May-97</td>
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<td>D</td>
<td>Aug-97</td>
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Organic C:N ratios were determined for samples from stations 7, 12 and 30 (Fig. 2.2d), using untreated sediment and sediment that had been rinsed in the desorption experiment. No change in C:N resulted from the desorption treatment, so C:N of untreated sediment was averaged with the C:N ratios of sediment used in each rinse. Deposited sediments averaged 10 to 14, and decreased upstream. Suspended sediments had C:N ratios averaging 7 to 10, with highest values in sediments from the station 12.

![Graph showing relationships between sediment organic material content (SOM; mg OM (100 mg sediment)^(-1)) and dissolved organic carbon (DOC; mg L^-1) for suspended (triangles; R^2 = 0.06) and deposited (circles; R^2 = 0.92) sediment.](image)

Figure 2.3. Relationships between sediment organic material content (SOM; mg OM (100 mg sediment)^(-1)), and dissolved organic carbon (DOC; mg L^-1) for suspended (triangles; R^2 = 0.06) and deposited (circles; R^2 = 0.92) sediment.

Specific surface area averaged 55 m^2 g^-1 sediment for suspended sediment, with a relatively narrow range of 52.4 to 60.0 m^2 g^-1. Deposited sediment had a lower average of 29 m^2 g^-1 sediment and a greater range of 18.9 to 35.1 m^2 g^-1 sediment. The
variation results from an increase in surface area as a function of estimated decrease in
grain size.

**Experimental effects**

Sediment releases of exchangeable organic carbon (EOC) varied systematically with sediment from different stations and different environments, as well as all four salinity treatments (Fig. 2.4). The first rinse yielded the most EOC in each case. The cumulative mass of EOC removed per gram of sediment showed highly significant differences ($p<0.0005$) in the main effects of environment, station and rinse salinity and their interactions (Table 2.2). The ANOVA included samples from stations 7 and 30, which were treated in exactly the same way. Data from station 12 sediments, which were sampled on a different date and rinsed only 1 h, are shown in Fig. 2.4 for comparison. The fresh (distilled) water experiment removed the most EOC from each sediment. The lower levels of EOC released by saline rinses of different ionic strength were not significantly different. Suspended sediment released more EOC than the bottom sediment, and the sediment collected in freshwater (station 30) released more EOC than the sediment collected in brackish water (station 7). The difference between EOC release by suspended and deposited sediment from station 12 was not as pronounced as that seen for sediment from stations 7 and 30. There was a high level of TSS when suspended sediment was collected, and the similarity between EOC values of sediment from the two environments may illustrate the effect of adding sediment from the deposit to the suspension.

The main effects of the treatments are modified by interactions that lead to subtle differences between the cumulative EOC released by each treatment and that
expected if the main effects were acting independently. If there were no interactions, the graph of station 7 suspended sediment EOC in Fig. 2.4 would be more similar in shape to the graph of deposited sediment EOC. In the suspended sediment, EOC of the 4 psu rinse is lower than that of both the 2 psu and the 16 psu rinses. However, the deposited sediment EOC of the 4 psu rinse is nearly as large as the EOC of the 2 psu rinse and somewhat larger than the 16 psu rinse. This is the most obvious indication of the interaction between environment and salinity. The EOC values of the 4 psu rinse of Station 30 suspended and deposited sediment shows nearly the same proportionality that other rinses show, indicating that the interaction also includes station effects. These interactions may indicate that response to any treatment variable
does not occur without modification by another variable. An alternative and equally likely possibility is that adding small amounts of OC in saline rinses and then correcting results by subtracting controls contributed a large error to cumulative totals. Discussion will be limited to the most obvious differences in organic material exchange caused by the main effects of environment, station and rinse salinity.

Table 2.2. Results of ANOVA on cumulative mass of organic carbon removed from sediment samples collected in May 1997.

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Sum of Squares</th>
<th>Mean Squares</th>
<th>F</th>
<th>Prob &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>collection environment</td>
<td>1</td>
<td>274.4</td>
<td>274.4</td>
<td>489.6</td>
<td>0.0001</td>
</tr>
<tr>
<td>station</td>
<td>1</td>
<td>48.8</td>
<td>48.8</td>
<td>87.0</td>
<td>0.0001</td>
</tr>
<tr>
<td>environment * station</td>
<td>1</td>
<td>28.6</td>
<td>28.6</td>
<td>51.0</td>
<td>0.0001</td>
</tr>
<tr>
<td>treatment salinity</td>
<td>3</td>
<td>219.5</td>
<td>73.2</td>
<td>130.6</td>
<td>0.0001</td>
</tr>
<tr>
<td>environment * treatment salinity</td>
<td>3</td>
<td>113.3</td>
<td>37.8</td>
<td>67.4</td>
<td>0.0001</td>
</tr>
<tr>
<td>station * treatment salinity</td>
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<td>17.9</td>
<td>6.0</td>
<td>10.7</td>
<td>0.0001</td>
</tr>
<tr>
<td>environment * station * treatment salinity</td>
<td>3</td>
<td>9.9</td>
<td>3.3</td>
<td>5.9</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

The significant effect of station on EOC levels of sediment from stations 7 and 30 may result from variations in the original SOM of sediment collected at different stations. Exchangeable OC is directly related to the original SOM for all stations included in the experiment (Fig. 2.5). Rinse water salinity and the environment from which sediment was collected modify the relationship. Suspended sediment (Fig. 2.5, A and B) had higher EOC for each increment of increased organic content than deposited sediment does (Fig. 2.5, C and D), after both fresh and saline treatments. Even when organic contents of suspended and deposited sediments are comparable, the suspended sediment releases more EOC. Salinity also reduces the EOC for each
sediment, resulting in lower slopes of the linear relationship to SOM (Fig. 2.5, B and D).

![Graph showing cumulative EOC as a function of original SOM](image)

Figure 2.5. Cumulative EOC is plotted as a function of the original SOM. Results show cumulative EOC after 5 rinses of sediment from each station for the following treatments: suspended sediment at a) 0 psu ($R^2 = 0.86$); b) suspended sediment at 16 psu ($R^2 = 0.42$); c) deposited sediment at 0 psu ($R^2 = 0.83$) and d) deposited sediment at 16 psu ($R^2 = 0.81$).

Treatments repeated 20 times show characteristics of early desorption similar to those seen in the short-term study (Fig. 2.6). The first rinse removes the most OM; subsequent rinses remove decreasing amounts that become nearly constant after about four rinses. The effect of salinity in limiting EOC was compounded in later rinses leading to divergence of EOC plots between 0 psu-treated sediment and 16 psu-treated sediment. The effect of environment was also compounded with one exception. Deposited sediment released less than 5 mg EOC/g sediment after 20 rinses. The
sediment collected from freshwater station 21 and treated in fresh water released ~10 mg EOC/g sediment.

A maximum of 31% of the original sedimentary organic carbon SOC was removed by 20 freshwater rinses of suspended sediment (Table 2.1). Other treatments removed less of the SOC. After 20 rinses at 16-psu, only ~14% of SOC was removed from suspended sediment and 4-13% was removed from deposited sediment. After five rinses a maximum of ~18% of SOC was removed. Much lower percentages are removed from deposited sediments (<5%) or by saline rinses (1-3%).

Figure 2.6. Cumulative totals of EOC removal after five and 20 rinses. Plus symbols refer to station 4, circles are station 7, crosses are station 21 and squares are station 30. Error bar is standard error of 2 replicates. Stations 4 and 21 were collected 8/97; stations 7 and 30 were collected 5/97.
Discussion

Control of sediment variation

The ANOVA determined statistically significant effects on sediment EOC of sediment characteristics labeled as station along the salinity gradient and suspended or deposit sedimentary environment. The variation in SOM of sediment collected at different locations may account for the station effect on EOC, because particles with higher original SOM clearly released a larger percentage during the experiment (Fig. 2.5). Using solvent extraction, Berger et al. (1984) removed more OM from suspended sediment, but did not observe the relationship documented here for OM exchanges in water. Sediment organic content is directly related to water column DOC concentration. Barataria freshwaters tend to have high DOC concentrations, so that both suspended and bottom freshwater sediments exhibit higher levels of SOM than sediment from saline environments (Fig. 2.2c).

The environment from which sediment was collected also affected the amount of OM adsorbed to sediment. The strong relationship between deposited sediment SOM and water column DOC (Fig. 2.3) is unexpected, given the weak relationship between suspended sediment SOM and DOC. The difference may be related to variations in the organic content or mobility of suspended and deposited sediment. Less EOC was released from deposited sediment even when its SOM is comparable to that of suspended sediment (Fig. 2.5, lines C and D). The nearly horizontal slope of this relationship indicates that the original SOM does not play a strong role at low levels. The low organic content of deposited sediment may approach a monolayer of organic molecules that cannot be removed (Mayer, 1994b). Suspended particles
contain proportionately more SOM than deposited particles, and experienced greater releases of EOC. The larger concentrations of SOM minimize interactions between mineral surfaces and the water, and organic material exchanges occur between other organic molecules and the water. Exchanges of organic material with water may occur more easily from other organic molecules than from mineral surfaces. This could allow more OM to go onto suspended sediment regardless of DOC and obliterate the relationship between DOC. It may also facilitate the greater release of EOC observed for suspended sediments.

Differing exposure to dissolved OM in the water column may also influence the desorption behavior of suspended and deposited sediments. Despite oscillations between oxidizing and reducing conditions in deposited sediment, the OM in near-surface sediments oxidizes at nearly the same rate as in continuously oxidized sediments (Aller, 1994; Aller et al., 1996). Organic carbon on deposited sediment may be repeatedly ingested and excreted by benthic feeders, without replenishment, depleting OM to a low level that is held tightly and protected from decomposition by its association with the mineral (Mayer, 1994b). Deposited sediment can be resuspended, but remains in one place long enough for the organic component to reach a stable balance with DOC in the overlying water. In contrast, suspended sediment travels through water of variable qualities, so that its organic component may never balance the DOM in the local water column. Sediment suspended in the water column may be colonized by bacteria or ingested and excreted, but it is returned to the water column where it accumulates new, possibly labile material. This is consistent with the
reports of increased numbers of bacteria and rapid metabolism on suspended aggregates (Alldredge and Silver, 1988).

Resuspended bottom particles act more like deposited sediments than suspended sediments in terms of their potential metabolic activity (Alber, 1997). No effort was made to distinguish these types of sediment in the desorption experiments. The suspended sediment load was high at station 12 (145 mg L\(^{-1}\)), which strongly suggests that sediments are being resuspended. It is unclear whether the low removal observed for suspended sediment from station 12 (Fig. 2.4) results from shorter rinse periods (1 h) or from the prevalence of resuspended bottom sediment that is inherently likely to release lower quantities of OM.

The variations in desorption and retention of OM by sediment collected in different parts of an estuary suggest a conceptual model that describes OM exchanges between particles and the water column (Fig. 2.7). Whether an organic molecule exchanges onto or off of a particle depends on the balance between DOC and the sediment organic content. Sediment particles accumulate higher levels of SOM if water column DOC is high, such as in freshwater draining nutrient rich uplands. They release organic material in water where DOC levels are lower, such as the coastal waters of the estuary. Deposited sediment maintains a balance with water column DOC that accommodates mineral adsorptive bonds with organic molecules, depletion of excess OM by benthic consumers, and limited replenishment with organic compounds from the overlying water. By virtue of its position in the water column, suspended sediment exchanges OM rapidly, and maintains higher levels of SOM than deposited sediment. With a thicker layer of OM, suspended sediment exchanges are
Figure 2.7. Conceptual model of organic material exchanges between sediment particles (parallelograms) and the water column, including the effects of sediment organic material and depositional environment and water column DOC. Circles are organic molecules dissolved in the water or adsorbed onto sediment. Plus symbols indicated ions in salt water. Straight thick arrows indicate organic material adsorption to sediment; Curved thin arrows indicate desorption from sediment. Organic exchanges occur in both directions between sediment and the water at all points. In freshwater where DOC is relatively high, suspended particles experience more adsorptive exchanges than desorption, so the particle accumulates a thick layer of organic material. Particles transported to saltwater also experience both adsorption and desorption, however, the balance in waters with low DOC favors desorption so organic material coatings become thinner as sediment EOC enters the water column. Deposited sediment in both locations experiences about the same number of adsorption and desorption exchanges but there may be more exchanges in freshwater where DOC levels are high and deposited sediment has higher SOM. The impact of this organic material exchange and transport mechanism on estuarine carbon cycling is determined by suspended load and DOC of the local water column.
more likely to involve bonds between organic molecules in multiple layers, rather than bonds between organic molecules and mineral grains. Exchanges occur more easily between suspended particles and solution, but sediment is likely to move from the area before SOM balances the DOC content of the local water column. The release of SOM may introduce a pool of organic material that is new to the location and of different lability from local DOC.

**Control of water quality**

Rinse water salinity also exerted a significant effect on the experimental release of sediment EOC. The most effective treatment used to remove SOM from sediment in this study was distilled water. This result parallels the finding in studies of adsorption that more OM will adsorb to sediment when salt is present in the water (Kirchman et al., 1989; Rashid, 1972; Preston and Riley, 1982), and is probably caused by a decrease in aqueous solubility of the OM at increased ionic strength (Thurman, 1985). However, rinses of different ionic strength did not remove statistically different amounts of SOM, suggesting that salinity is not the primary factor controlling SOM removal in this study or the organic exchanges of estuarine sediment grains.

Water quality factors that contribute to the experimental effect of salinity include DOC concentration and pH. The pH of distilled water used in the experiments was near 7, and rinse solutions made from synthetic seawater had a higher pH (~9), closer to that of seawater. In distilled water, the lower pH causes the increase in OM solubility noted above, while the low concentration of electrolytes encourages the release of organic molecules to buffer the solution. The higher pH of the salt water
decreases the solubility of organic molecules and buffers the solution. Any inorganic or organic molecule dissolved in the estuarine water column may inhibit OM being released into the water column.

DOC levels may exert a more systematic control on sediment-OM exchanges than salt content. Kirchman et al. (1989) suggested that the presence of OM in natural waters changes experimental conditions and therefore results. The saline rinses used here contained small amounts of DOC contributed by the Instant Ocean which were proportional to the rinse salinity. The reduction of EOC released from sediment in saline (OM-containing) rinses may be related as much to DOC concentration, as to the electrolytes in the water. If this is true, then water relatively depleted in OM will remove more OM from sediment than water of similar or higher organic content. Similarly, water with high DOC maintains the present concentration of SOM or exchanges OM onto sediment to enrich SOM. This idea is consistent with the results shown in Fig. 2.3.

In the estuarine model, sediment moving from fresh to marine environments experiences increases in pH and salinity, often accompanied by a decrease in DOC (Fig. 2.7). The combination of changes in pH, DOC and salinity allows the accumulation of OM onto sediment in freshwater environments. When the particle is transported to saline environments, the SOM is depleted as organic molecules desorb from particles to balance lower levels of DOC.

**Organic exchange process**

The types of interaction between sediment and OM include electrochemical interactions between the two surfaces, and hydrophobic expulsion from the solvent
(Westall, 1987). Although ligand exchange controls adsorption onto metal oxides in soils (Tipping and Cooke, 1982), hydrophobic interactions are said to control the adsorption and desorption of OM from aluminosilicate mineral grains (Zutic and Tomaic, 1988). This term refers to the attraction of water molecules for each other as well as the repulsion of non-polar molecules from water, and results from the tendency of non-polar constituents in water to meet and join (Cosovic and Vojvodic, 1989). Solutions of low ionic concentration are less polar than saline solutions. As a result, organic molecules are likely to desorb from particles when exposed to fresh water. Rinses removed OM that was not likely to be in direct contact with the mineral grain, because OM remained on sediment after the treatments. OM directly adsorbed onto a hydrophilic surface renders the surface hydrophobic (Murphy et al., 1990), so lower layers of OM may be bonded by a different mechanism. The release of organic molecules, whether they are in contact with mineral grains or other organic molecules is related primarily to what is already in the rinse water and what is available on the sediment. Water that is most depleted in ions takes up new material most readily, and sediment covered with the most SOM relinquishes its outer layers most easily.

A zero level of removal was not reached during this experiment. The most effective treatments removed ~18% after five rinses, and ~30% after twenty rinses. Projecting the 20-rinse removal rates indicates it would take 150-200 rinses to remove all SOM; this is 75-100 days for 12 h rinses. Park (1998) estimated that materials take ~60 days to travel from station 30 to the mouth of Barataria Bay, but it is unlikely that they would be subject to complete removal of SOM. Suspended particles in an estuary encounter continuously changing water quality quite different from treatments
described here, and they exchange continuously to adjust to local conditions. Organic-free sediment exposed to natural seawater is quickly coated with an organic film (Hunter, 1980). Consequently, the lower limit of removal probably falls above 0% organic content, possibly to the level of one layer of organic molecules bonded directly to mineral faces. For suspended and deposited sediments with surface areas averaging 55 m² g⁻¹ and 29 m² g⁻¹ this would be about 44 mg OC g⁻¹ sediment and 23 mg OC g⁻¹ sediment or 4% and 2% (Mayer, 1994).

Fractionation can occur in adsorption of organic molecules onto mineral grains and removal from mineral grains. In hydrophobic attachments the least soluble organic compounds will be most highly sorbed (Thurman, 1985), such that high molecular weight, low solubility fatty acids may be preferentially adsorbed (Hedges, 1977). Desorption might, therefore, be expected to select hydrophilic groups. There is no change in C:N ratios of sediment before and after desorption treatments (Fig. 2.2d). This suggests that desorption is not selective. However, the measurement of C:N lacks sensitivity because remaining OM dominates the chemical signature of SOM. Continuing the treatments beyond five rinses might have indicated selectivity by desorption. There are clear differences among C:N ratios of sediment from different locations that indicate either selectivity or downstream variations in the source of organic material. Preferential selection could arise from continued OM exchanges or from modification of adsorbed SOM. The increase of C:N ratios from suspended to deposited sediment indicates selective removal of nitrogen-containing compounds, and shows that organic material preserved in deposits is likely to be relatively enriched in carbon.
Importance of sedimentary carbon in water column cycling

Exchangeable organic carbon may provide a source of organic material to the water column that differs from DOC in lability and contributes to OM cycling within the estuary. The SOM released during desorption experiments was converted to a production measurement by multiplying EOC by the corresponding suspended sediment load, and assuming 2 m water depth (Fig. 2.8). This estimate does not represent primary production, and the measurement was not normalized per day (treatments lasted 5 h-10 d), but it allows comparison between EOC and other sources of OC including primary production. Phytoplankton production in the bay averages 0.5 mg C m\textsuperscript{-2} d\textsuperscript{-1} (Day et al., 1989). The actual production of OC depends on local conditions and varies between 0.0 and 1.5 mg C m\textsuperscript{-2} d\textsuperscript{-1} (Day et al., 1989). The carbon released by the treatments were on the same order as primary production of carbon (Fig. 2.8a). Repeated rinsing (20 times) and freshwater rinsing caused sediment to release the most carbon by sediment weight, however sediment of moderate organic content (stations 4 and 12) introduced the most carbon into the water. Resuspension led to a high suspended load at station 12, so the released carbon could make a larger impact on the water column than any of the other sedimentary inputs. In addition, the water at stations 12 and 4 has low DOC, so the SOM that is removed from grains may contribute a larger amount to that available in the water column (Fig. 2.8b). The generally lower DOC of saline waters near the mouth of Barataria Bay allows for a greater effect of removed SOM in this part of the estuary than in more organic-rich freshwater regions. This exercise illustrates how local DOC and suspended load are as
important in determining the effect of sediment organic releases as the amount of carbon that can be removed from a unit weight of sediment.

Figure 2.8  a) Organic carbon removed from the sediment expressed as production (g OC m$^{-2}$), assuming a water depth of 2 m. These numbers are not normalized to a daily production; rinse treatments lasted a total of 5 h to 10 d. Average phytoplankton production ranges 0-1.5 g OC m$^{-2}$d$^{-1}$. The upper line is the maximum value; the lower line is the average value (Day et al., 1989). b) Organic carbon removed from sediment expressed as a percentage of water column DOC. Large symbols are 20 rinse totals; small symbols are 5 rinses totals. Circles are 0 psu, up-triangles are 2 psu, down-triangles are 4 psu, and squares are 16 psu. Each point corresponds to the station whose number is above it.
The basic mechanism by which sediment can transport organic material from regions of high productivity to less productive areas is shown in Fig. 2.7. In this model sediment acquires high levels of SOM in water with high DOC and then releases OM into waters with low DOC. The quantitative importance of released organic material to an estuarine location is determined by local DOC and suspended load.

Conclusions

Desorption experiments indicate that sediment organic content and collection environment have a significant effect on the levels of exchangeable organic material (EOC) released by sediments. The quality of the rinse water (including pH, salinity and DOC concentration) also controls the exchanges. These results suggest a model whereby suspended material in the estuary provides a transport mechanism for organic material from regions of high productivity to locations relatively depleted in DOC. Deposited sediment carries a low percentage of SOM that, for the sediments described here, was closely related to DOC concentration. Suspended sediment has much thicker organic coatings and the concentration of SOM is not related to DOC concentration. As suspended sediment moves through highly productive freshwater, it accumulates OM in water with high levels of DOC. When it reaches salt water environments characterized by lower productivity, the suspended sediment may shed organic molecules to water relatively depleted in DOC. The treatments described here did not continue long enough to distinguish changes in C:N ratios of organic material remaining on sediment, but differences among C:N of different sediments indicate such selection does occur along the salinity gradient and may lead to selective
transport and preservation of high carbon content organic molecules in estuarine sediments. Sediment exchange can introduce a source of organic material to the water column that is new to the location, comparable in magnitude to primary production by phytoplankton, and possibly more labile than local DOC.
CHAPTER 3
MICROBIAL UTILIZATION OF ESTUARINE DISSOLVED AND SEDIMENTARY ORGANIC MATERIAL

Introduction

The adsorption of organic material to mineral grains has been suggested as a mechanism of preserving labile carbon in continental shelf deposits (Keil et al., 1994a; Mayer, 1994b). The dependence of organic material preservation on its attachment to mineral sediment transported from primarily terrestrial sources introduces speculation about the source and characteristics of the preserved organic molecules (Lee, 1994a). Attention focuses on estuaries as a site where transformations and exchanges of mineral bound organic material occur that control which organic molecules are transported offshore and ultimately deposited as sedimentary organic material (Henrichs, 1995; Lee and Wakeham, 1992; Chapter 2).

The lability of dissolved organic material has been shown to depend on many things, including nutrient concentration and source (Coffin et al., 1993; Kroer, 1993; Zweifel et al., 1993). It is questionable whether an organic molecule that is attached to mineral grains is more or less likely to be consumed than a similar unattached molecule. Studies that examined nutrients and proteins on glass showed that adsorbing compounds on a surface may facilitate microbial consumption by concentrating organic material and exposing its bonds to hydrolysis (Taylor, 1995; ZoBell, 1943). However some studies have shown that adsorption hinders the consumption of organic material (Nagata and Kirchman, 1996). Different clay minerals have affinities for specific functional groups on organic material that can strengthen certain bonds and lead to preferences in preservation and utilization of...
various organic molecules (Dashman and Stotzky, 1986). In a study using both natural sediment and natural organic material, Keil et al. (1994a) documented the degradation of desorbed organic material from a continental slope sediment deposit.

This work examines the biological availability of different pools of estuarine organic material. Bacteria growth on dissolved organic material and organic material carried by estuarine suspended and deposited sediment is compared. The organic materials used as substrate and the bacteria populations added to consume the organic substrates are natural assemblages that exhibit diversity in composition. The experiments were conducted in two different locations in the estuary and on several different dates to examine how changes in water quality influence the use of different pools of organic material.

Methods

Site description

Barataria Bay lies in an interdistributary basin in Louisiana, bounded to the north and east by the Mississippi River, to the west by Bayou Lafourche and to the south by Grand Isle, a coastal barrier island (Fig. 3.1). The watershed is in a temperate climate and supports agricultural fields, cypress-tupelo swamp, and fresh, brackish and saline marshes. The estuary is shallow (~2 m deep) and well-mixed. Sediment is imported to the estuary by drainage of upland environments, and imported from the continental shelf of the Gulf of Mexico. Sediment is also redistributed within the estuary by resuspension, and lateral transport during the passage of seasonal storm fronts.
Figure 3.1. Map of Barataria Bay, Louisiana showing inland station (labeled 30) and coastal station (labeled 4) where samples were collected to compare the bacterial uptake of dissolved organic material and sedimentary organic material.

Water quality

Samples were collected from inland and coastal locations in Barataria Bay in February, June and August 1998. Surface water (500 mL) was collected with a bucket, stored on ice and returned to the laboratory for water quality analyses. Salinity was measured using a conductivity meter. Total suspended sediment was determined as the weight of a rinsed sample remaining on a filter (Whatman GF/C,
mesh diameter 1.2 μm) after drying at 60°C for 24 hr, divided by the volume of the sample. Filtered water samples (Whatman GF/F, mesh diameter 0.7 μm) were analyzed for dissolved organic carbon (DOC) on a Shimadzu TOC5000A using platinum-catalyzed oxidation at 670°C. The particulate organic carbon (POC) concentration was measured as the difference between carbon analyses on raw and filtered samples. The concentration of chlorophyll a was estimated using fluorescence after extracting the pigment from phytoplankton in a solution of 90% acetone 10% dimethyl sulfoxide (modified from EPA method 445.0, (Arar and Collins, 1992).

**Experiments**

Surface water for dissolved organic material incubations was collected with a bucket, stored on ice in acid-washed (10% HCl) polyethylene containers, and processed the same day in the lab. Bottom sediment was collected during February and June using an Eckman dredge, stored on ice and refrigerated upon return to the lab. Large samples of surface water (~100 L) were collected, refrigerated in the laboratory, and allowed to sit undisturbed for 24 hours. The overlying water was siphoned off, and the remaining water and sediment were centrifuged to separate the sediment used in the experiment.

Dissolved organic material (DOM), and sedimentary organic material (SOM) from both suspended and deposited sediment were incubated with bacteria to measure the microbial uptake of DOC. The experimental design was adapted from a procedure described for batch cultures of DOM (Kroer, 1993). All containers and membrane filters used in the experiment were washed in 10% HCl, and glass fiber filters were ashed at 550°C for one hour to minimize the introduction of bacteria.
Surface water was sequentially filtered through 0.7 μm (Whatman GF/F), and 1.0 and 0.2 μm (Nuclepore polycarbonate membrane) filters within hours of returning from the collection site, to obtain the DOM growth medium. For the inoculum, sample water was filtered through 1.0 μm membrane filters that allowed most bacteria to pass, but retained most bacteria predators. Duplicate 500 mL flasks each held 450 mL of DOM growth medium and 50 mL of the inoculum. Duplicate control flasks holding 450 mL of distilled water and 50 mL of inoculum were used to document the effect of the inoculum on changes in bacteria and carbon concentrations.

Experiments using deposited sedimentary organic material (SOM-D) were initiated the day after collection. Organic material was removed from sediments and added into distilled water in the following manner. Bottom sediment was subdivided into 10 50-mL centrifuge tubes, dispersed in ~30 mL of distilled water, agitated for one hour, and centrifuged. The overlying water from each tube was siphoned into a container and stored in the refrigerator. The rinse was repeated twice and the rinse water from all three rinses was mixed to provide ~900 mL of SOM growth medium. This solution was divided into duplicate 500 mL flasks which were then inoculated with bacteria using 50 mL of 1.0 μm filtered water from the corresponding station. Duplicate controls holding 450 mL of distilled water and 50 mL of the inoculum were established with each SOM treatment.

The treatments for suspended sedimentary organic material (SOM-S) were initiated two days after sample collection using the sediment that was concentrated by settling and centrifugation. The growth medium was obtained using the desorption
procedure described for SOM-D. Duplicate experimental and control flasks were set up in the same way as described for DOM and SOM-D.

Incubations were stored at room temperature (~26°C) in the dark and sampled eight times at approximately 0, 12, 24, 48, 72, 96, 144 and 192 hr. At each sample time 10 mL were preserved with 0.5 mL of formaldehyde and refrigerated for bacteria counts, and ~20 mL were frozen for carbon analysis as described above. The concentration of bacteria in preserved samples was counted using direct counts of acridine orange stained samples under epifluorescence microscopy (Parsons et al., 1984a). A minimum of 10 fields or 300 cells were counted in each sample.

This basic procedure was used to run experiments for DOM incubations of samples from the coastal station in February, July and August, and from the inland station in August. Incubations of SOM-D and SOM-S were likewise run in February and July for both freshwater and saltwater stations.

The effect of microfaunal grazing of bacteria was considered in experiments using DOM from samples collected at the coastal station during June. One set of flasks excluded bacteria as described above. In addition, a treatment that included bacterivores was established using duplicate flasks containing the DOM growth medium (450 mL) and an inoculum of untreated water (50 mL), rather than the 1.0 μm filtered inoculum that excluded predators. This grazer treatment had a different inoculum from the bacteria-only DOM treatment, so a corresponding control of raw water inoculum with distilled water medium was prepared in duplicate.
Data analysis

Differences among treatments were examined using changes in bacterial abundance and carbon concentration. Each replicate measurement of carbon concentration or bacteria abundance in the treatment flasks was adjusted by subtracting the average of the two corresponding measurements for control flasks. This gave two replicate series of carbon and bacteria measurements for each treatment. For each series, the initial bacteria count was subtracted from each subsequent count and the largest value was called the net growth of the bacteria population. The variation of log transformed values of net growth was analyzed using a three-way factorial analysis of variation (ANOVA) with the following factors: collection station, organic material substrate and month of the experiment (SAS Institute, 1996). Significant factors were distinguished with Type III sums of squares because of missing data for DOM experiments (Freund and Wilson, 1993).

The amount of carbon incorporated into bacterial biomass by the net growth in bacteria numbers was estimated using the average bacteria cell volume (0.21 μm³) and conversion factor (350 fg C μm⁻³) reported by Bjornsén (1986). The conversion factor accounts for the carbon content, density and ratio of wet to dry weight bacterial biomass (Bratbak, 1988). The estimated carbon associated with bacteria biomass was compared to organic carbon loss in flasks using simple linear regression (SAS Institute, 1996). The instantaneous growth rate of bacteria was calculated during each sample interval by solving for r in the exponential growth equation \( P_2 = P_1 e^{\Delta t} \). In this equation \( P_1 \) is bacteria abundance observed at the start of a sample interval, \( P_2 \) is
bacteria abundance at end of the interval, and $\Delta t$ is the time length of the interval in hours.

**Results**

**Water quality**

The water column salinity ranged between 16.4 psu and 22.0 psu for the coastal station and was always < 0.5 psu at the inland station, with the highest salinity observed at both stations in August (Table 3.1). The total suspended sediment (TSS) concentrations were highest at both locations in February (32 mg L$^{-1}$ at the coastal station, 50 mg L$^{-1}$ at the inland station), and lowest in August (coastal, 15 mg L$^{-1}$; inland, 10 mg L$^{-1}$). The concentration of DOC was higher at the inland location, which had its lowest DOC content in June (7.5 mg L$^{-1}$), and its highest in August (13.9 mg L$^{-1}$). By contrast, the coastal station had the highest DOC concentration in June (5.1 mg L$^{-1}$) and the lowest in August (3.2 mg L$^{-1}$). Both stations had moderate DOC values in February. The highest POC concentrations were observed in August. The lowest POC measurement at the coastal station was in February (0.6 mg L$^{-1}$); the lowest measurement for the inland station was observed in June (0.0 mg L$^{-1}$).

Chlorophyll $a$ values were higher at the inland station than at the coastal station, while both exhibited their highest values in June and lowest values in August.

**Experiment results**

The results of the experiments on suspended sediment organic material (SOM-S) from the coastal station can be used to illustrate the variability observed between replicates and between treatment and control for bacterial abundance and DOC concentration (Fig. 3.2). The exponential increase in bacteria density is typical of
Table 3.1. Water quality at sites where water and sediment were collected. TSS is the concentration of suspended sediment, DOC is dissolved organic carbon (1.2 mm filtered), POC is particulate organic carbon (difference between carbon measurements on raw and filtered water samples), and Chl a is chlorophyll a.

<table>
<thead>
<tr>
<th>Station</th>
<th>Date</th>
<th>Salinity</th>
<th>TSS</th>
<th>DOC</th>
<th>POC</th>
<th>Chl a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barataria Bay (coastal)</td>
<td>18-Feb</td>
<td>19.7</td>
<td>32.1</td>
<td>4.83</td>
<td>0.58</td>
<td>14.46</td>
</tr>
<tr>
<td></td>
<td>30-Jun</td>
<td>16.4</td>
<td>22.4</td>
<td>5.19</td>
<td>1.01</td>
<td>25.70</td>
</tr>
<tr>
<td></td>
<td>5-Aug</td>
<td>22</td>
<td>15.4</td>
<td>3.2</td>
<td>5.59</td>
<td>2.40</td>
</tr>
<tr>
<td>Bayou des Allemands</td>
<td>18-Feb</td>
<td>0</td>
<td>50.3</td>
<td>11.38</td>
<td>2.55</td>
<td>29.53</td>
</tr>
<tr>
<td>(inland)</td>
<td>30-Jun</td>
<td>0.5</td>
<td>12.8</td>
<td>7.54</td>
<td>0</td>
<td>35.96</td>
</tr>
<tr>
<td></td>
<td>5-Aug</td>
<td>0.5</td>
<td>10.2</td>
<td>13.91</td>
<td>3.94</td>
<td>15.00</td>
</tr>
</tbody>
</table>

bacteria growth in cultures (Parsons et al., 1984b). The coincident decline in DOC concentration with increasing bacteria density indicates bacteria consumption of the organic substrates provided in the treatments (e.g., 3.2 a, c). Large differences between the bacteria abundance in treatment flasks and control flasks indicate that bacteria utilized the detached sedimentary organic substrate for growth and were not solely reliant upon the organic material in the inoculum (Fig. 3.2 a, b). The bacteria density in replicate flasks was in good agreement, in the example shown and in other treatments, although the timing of an increase or decrease may have differed between replicates. The variability between replicate DOC analyses was similarly low in February experiments (Fig. 3.2c), but high in June experiments (Fig. 3.2d). In February experiments DOC measurements in treatments were higher than in controls, similar to the pattern of bacteria density. The high variability of DOC measurements in June obscured this effect. Increases and decreases in both the treatment and control
flasks in June indicate that processes other than bacteria assimilation, such as predator-prey interactions and abiotic oxidation, control the transformations between dissolved and particulate pools of organic material.

![Graphs showing experimental concentrations of bacteria and DOC for suspended sediment organic material from the coastal station in February and June, showing variation between two replicates and between experimental flasks and control flasks.](image)

**Figure 3.2.** Experimental concentrations of bacteria and DOC for suspended sediment organic material from the coastal station in February and June, showing variation between two replicates and between experimental flasks and control flasks. The high variation in DOC measurements between replicates in June experiment was checked by a repeated analysis that yielded similar results.

The patterns observed in experiments on SOM-S typify the results from incubations of all organic media. All flasks showed a growth in bacteria abundance within 96 hr, but the amount of growth and its timing varied. After 96 hr, the variation
between replicates increased and the changes observed in flasks could not be attributed only to DOC consumption by bacteria. The results for the first 96 hr were summarized by averaging replicate cell counts after they were corrected for the number of bacteria in controls (Fig. 3.3). The bacteria density increased in all flasks indicating that bacteria growth uses all substrates: DOM, SOM-S and SOM-D. The amount of growth varied, in part because the flasks contained different initial numbers of bacteria. The flask containing dissolved organic material contained the lowest numbers of bacteria initially (~4-0.72 x10^6 cells mL^-1) and at their maximum levels (1.6-3.7 x10^6 cells mL^-1). Flasks with SOM-S had the highest initial numbers (12.6-19.7 x10^6 cells mL^-1) and the highest maximum counts (38.2-56.6 x10^6 cells mL^-1) of bacteria. Flasks containing SOM-D had initial bacteria density and growth between these two extremes. Initial values were 0.02-4.0 x10^6 cells mL^-1, and maximum counts were 1.3-6.4 x10^6 cells mL^-1. The maximum bacteria abundance was reached at an earlier hour in June and August than in corresponding February incubations. In general there was good agreement between replicates for the first 24 hr of each experiment, and higher variation after that. The exception to this pattern was observed in the SOM-D flask from the inland station, which showed high variability between replicates throughout both the February and June experiments.

Similarities were observed in the bacteria growth patterns on different substrates. Bacteria density increased during the first 72-96 hr on all types of OM substrate. Bacteria density decreased at 12-24 hr in both SOM substrates from the inland substrate, but then increased again (Fig. 3.3 d, f). The bacteria density reached higher levels on DOM and SOM-D substrates in June than in February (Fig. 3.3 a, c,
d). All SOM-S flasks exhibited their highest counts in the February growth experiments. Bacteria growth was higher on the inland DOM sample than the coastal DOM sample in the August experiments.

![Graph showing bacterial growth trends for different samples](image)

Figure 3.3. Trends in bacteria growth for treatments of dissolved organic material (DOM) and sedimentary organic material from the deposit (SOM-D) and suspension (SOM-S). Symbol represents the average of two replicates minus the average of two controls. Circles represent February data, squares represent June data, and crosses represent August data. Notice the difference in vertical scale for each type of organic material substrate.

All February incubations showed declines in DOC (Fig. 3.4), but DOC changes were not temporally coherent with bacterial growth and declined in the summer experiments (see Fig. 3.3). In February most flasks showed small declines in OC from initial maximum values of 1.2-3.3 mg L\(^{-1}\) to minimum values of 0.8-2.7 mg
This loss amounted to 11% of the carbon in DOM, 43-53% of carbon in SOM-D, and 65% of the carbon in the inland SOM-S sample. The coastal SOM-S showed a larger decline in carbon during February, dropping 79% from 7.0 mg L\(^{-1}\) to 1.5 mg L\(^{-1}\). The DOC concentrations in June and August experiments treatments showed both increases and decreases, suggesting complex carbon dynamics. The DOC concentration in the SOM-S experiments from both stations decreased, dropping from

![Graph showing carbon concentration trends for DOM, SOM-D, and SOM-S in coastal and inland stations.](image)

Figure 3.4. Trends in carbon concentration for treatments of dissolved organic material (DOM) and sedimentary organic material from the deposit (SOM-D) and suspension (SOM-S). Error bars indicate the standard deviation of two replicates. Replicates were obtained by subtracting the mean carbon concentration of two control flasks. Circles represent February data, squares represent June data, and crosses represent August data. Numbers on the graph indicate the percentage of DOC lost by the hour at which the number is placed.
maximum values of 2.4 and 13.7 mg L\(^{-1}\) to values equal to that in the control flasks at 96 hours. The experiment on inland SOM-D also showed an initial 51% decline in DOC from a maximum of 15.8 mg L\(^{-1}\), but increased after reaching a minimum of 7.7 mg L\(^{-1}\) at 22 hours. Coastal samples of DOM and SOM-D increased in DOC from initial values of 4.0 and 4.3 mg L\(^{-1}\) to maxima of 5.2 and 11.1 mg L\(^{-1}\) respectively. The August experiment on DOM showed initial decreases of DOC from 3.8 and 6.0 mg L\(^{-1}\) to minima of 0.0 mg L\(^{-1}\) (46 hours) and 4.6 mg L\(^{-1}\) (14 hours), for coastal and inland stations respectively. Both DOM treatments increased beyond initial carbon concentrations. Consistent DOC losses in all February experiments and June SOM-S experiments are assumed to be associated with the observed increases in bacterial abundance. However, summer changes in DOC concentration are not clearly related to the changes in bacterial abundance.

The June grazer experiment demonstrated microbial consumption of the bacteria growing on the DOM substrate (Fig. 3.5). The initial bacteria abundance was higher in both treatment and control flasks that included grazers, because bacteria were added with the grazer inoculum. Net growth (corrected by subtracting control population) was higher in flasks that excluded grazers \((3.6 \times 10^6\) cells mL\(^{-1}\)) than grazed flasks \((0.7 \times 10^6\) cells mL\(^{-1}\)). The most rapid growth occurred later in grazer-excluded flasks (24 hr) than grazed flasks (14 hr), but both treatments reached a peak abundance at 47 hr. The grazed population subsequently declined, while the ungrazed population maintained a high density at 68 hr.

The analysis of variance showed that neither collection date nor sample station significantly affected net growth, but that the type of organic substrate was highly
Figure 3.5. Changes in bacteria abundance in the June grazer experiment on dissolved organic material substrate. Flasks contained either a raw water inoculum (bacteria and grazers) or a 1.0 μm filtered inoculum (bacteria only). Each symbol represents the average of two replicates; the error bar indicates one standard deviation.

significant in determining the variation (p = 0.0001). The SOM-S substrate supported the highest net growth in bacteria (Fig. 3.6). The highest growth in bacteria abundance was observed in the February experiments of coastal SOM-S (58 x10^6 cells mL^-1). Other SOM-S treatments yielded between 7.1 and 30 x10^6 cells mL^-1. The maximum growth on DOM and SOM-D substrates was between 1.6 and 5.3 x10^6 cells mL^-1; these treatments were not significantly different from each other. In most cases the substrates collected in coastal locations supported greater bacterial growth than substrates from the inland site. That difference was large for results from the SOM-S experiments in both February and June. This led to a significant interaction of substrate with collection date (p=0.020), and a marginally significant interaction of substrate with sample location (p=0.057). Exceptions to the general pattern occurred in the August DOM experiment (the only DOM experiment for inland substrates), and February SOM-D experiments in which the bacteria growth was moderately higher on inland substrates than coastal substrates.
Figure 3.6. Maximum net growth (cells mL$^{-1}$) and maximum instantaneous growth rate (cells hr$^{-1}$) of bacteria. a) Net growth for dissolved organic material (DOM), and sedimentary organic substrates from the deposit (SOM-D) and suspension (SOM-S); b) Instantaneous growth rate for dissolved and sedimentary organic substrates.

The instantaneous growth rate (IGR) was generally higher in flasks containing substrates from the coastal location. The IGR decreased from February to June except in the DOM experiment and the SOM-D experiment for inland samples. The highest IGR was observed for SOM-D collected from the coastal location in February (0.27 hr$^{-1}$). It was also relatively high for DOM substrates (0.12-0.18 hr$^{-1}$).

The correlation between the net growth of bacterial numbers and organic carbon losses from experimental flasks uses bacteria numbers converted to a bacterial
Figure 3.7. Estimated gain in bacterial biomass associated with the observed loss of carbon in incubations. DOM refers to dissolved organic material substrates; SOM-S is sedimentary organic material from suspended sediment and SOM-D is sedimentary organic material from deposited sediment. Summer incubations that showed carbon gain during the experiment are not shown. The regression line is fit to February data only (p=0.0002).

Biomass estimate to maintain consistent units (Fig. 3.7). The regression model is not significant for June and August samples (p=0.25). However, the estimated changes in bacterial biomass correspond well to carbon loss in February, leading to a highly significant linear relationship (p=0.0002, $R^2=0.85$). Several lines of evidence suggest that bacterial incorporation of carbon into biomass varies with substrate type. Although results from DOM experiments plot close to the regression line, SOM-D...
results fall below the line and SOM-S results fall above the line. The difference in the location of theses points indicates that bacteria require more carbon from SOM-D than SOM-S to produce a given quantity of biomass. The conversion from net growth to biomass assumes that all cells are the same size. Observations of cells under epifluorescence microscopy also indicate that the bacteria growing on SOM-S source material were approximately five times larger than those growing on other substrates. Both the increased bacteria size per cell and the greater biomass per carbon loss of bacteria in the SOM-S substrate suggest that bacteria incorporate carbon more efficiently from the SOM-S substrate than other labile materials.

Discussion

Substrate lability

Organic material from both dissolved and sedimentary sources is clearly bioavailable, because both substrates support the growth of bacterial populations larger than was observed in control flasks. A relatively small, labile component of the ambient DOC, ~0.1-3%, supports bacteria growth in natural aquatic environments (Coffin et al., 1993). Higher percentages of DOC are consumed in laboratory experiments such as these. If we assume that all carbon lost in February experiments was consumed by bacteria, then 11% of the organic carbon in DOM is available, which is similar to the 5-9% of DOC consumed in uptake experiments conducted in coastal Florida (Kroer, 1993). The increased bacteria growth on DOC when nutrients are added indicates that utilization of otherwise labile DOC may be limited in some environments (Zweifel et al., 1995).
The observations of bacteria growth and carbon loss for the incubations described here indicate that organic material removed from sediments can supplement bacteria growth and may be important when labile DOC is limiting in the environment. Proportionally more SOM than DOM was used by microbial consumers. Organic material from deposited sediment (SOM-D) supported bacterial populations of the same magnitude as the populations supported by DOM, but used 43-53% of initial carbon supply (Fig. 3.4). This rate of use is lower than the 90% loss of carbon that Keil et al. (1994b) attributed to microbial use of organic material from continental shelf surface sediments. Differences between the methods used or the sampling locations can cause large differences in results. Organic material from suspended sediment (SOM-S) declined in carbon by 65-100%. This carbon loss coincided with the largest growth in the bacteria population observed in this study. The percentage of carbon loss, coupled with high growth of bacteria populations, suggests that suspended sediment provides the most labile of the substrates examined here. In addition, bacterial growth efficiency is highest in populations grown on the SOM-S substrate (Fig. 3.7). An increase in bacterial growth efficiency indicates that biomass production is more important relative to respiration in bacterial utilization of DOC (del Giorgio and Cole, 1998). These results indicate that the organic substrate available on suspended sediment may be a significant source of organic carbon to water column consumers.

The high percent of utilization of SOM-S may be a consequence of its composition. Suspended sediment collected throughout the basin generally has higher N content than deposited sediment (Chapter 4), which has been shown to improve the
growth efficiency of bacteria on organic material (Kroer, 1993). Therefore, compositional differences in organic material attached to mineral grains in the suspension may cause it to have higher lability than organic material attached to deposited sediment. Continuous exchanges of organic material between suspended sediment and the water column (Chapter 2) may encourage adsorption of more easily utilized compounds, or the sediment may be transported from the location before its labile, attached, organic components can be used. Either way, SOM-S maintains a high percentage of labile organic material. This distinguishes it from DOM and SOM-D, which are depleted of labile organic material.

Although a high proportion of the SOM-S is labile, and bacteria appear to use it more efficiently, the consumption of SOM by bacteria does not quantitatively approach that of DOM in natural environments. There is much more DOM present in a given volume of water. While the DOM used in the experiment was filtered and used at its field concentration, the organic material taken from suspended sediment was concentrated from a 100 L water sample. If the DOC concentration at a station is multiplied by its percentage of uptake, it appears that 0.3-4 mg C L⁻¹ were available for microbial consumption as DOM. The organic material from suspended sediment amounted to only 0.01-0.02 mg C L⁻¹ at the inland location, and 0.05-0.14 mg C L⁻¹ at the coastal location when the experiments were conducted. The amount of sedimentary organic material available on a given day depends on the suspended sediment concentration and the organic content of the suspended sediment. While DOM provides the majority of organic carbon to bacteria, the organic material on
suspended sediment can be a significant component of the estuarine carbon cycle, particularly when DOC is limited or its lability is low.

The incubations used here separated organic material from sediment prior to exposing it to bacteria. Adsorption increases the remineralization rate of organic material in solutions containing low concentrations of labile substrate (Taylor, 1995), at least in part because it concentrates the organic material on surfaces (ZoBell, 1943). High concentrations of DOC are usually observed in estuaries (Day et al., 1989), so the bacteria may have access to dissolved as well as sedimentary organic material. The attachment to mineral grains in this case may offer some protection from bacterial consumption (Dashman and Stotzky, 1986; Nagata and Kirchman, 1996). Given the exchanges that are likely to shift organic material between adsorbed and detached states (Chapter 2), it is likely that some of the organic material that is tested here will be detached elsewhere in the estuary and made available to bacteria as dissolved organic material. In addition, the utilization of mineral-attached labile organic molecules may encourage the consumption of less choice organic components that are also attached. The adsorption of labile organic compounds to colloidal organic material increases the use of the less labile colloidal material just as it reduces the consumption of the labile component over the amount taken up from DOM (Schuster et al., 1998).

Seasonal and spatial variation in uptake characteristics

Although the main effects of station and date were not significant factors determining the variation of net bacteria growth, both interacted with substrate to modify its highly significant effect. The interaction between date and substrate results
from a difference among substrates in how bacteria net growth changes from February to June and August. There was little variation among months in the maximum net growth of bacteria in dissolved or deposited sediment organic substrates. However, the suspended sediment organic material showed a large decrease in the maximum net growth from February to June that caused the interaction of collection date with substrate type in the ANOVA. The instantaneous growth rate (IGR) shows a similar decrease from February to June for corresponding locations of suspended sediment organic material, as well as deposited sediment organic material from the coastal location. But the IGR decreased in experiments using inland deposited sediment organic material and coastal dissolved organic material increase from February to June. Another prominent difference among results from different months was the shift from a strong February correlation between bacteria growth and carbon loss in the flasks, to a complete absence of correlation between the two variables in summer experiments.

There is little relationship between IGR and measured water quality parameters of salinity, suspended sediment concentration and dissolved organic carbon concentration. In addition the IGR, which is usually directly related to temperature (White et al., 1991), decreased from winter (February) to summer (June) in experiments using all suspended sediment organic substrates and the deposited organic material from the coastal location. The absence of a direct relationship between instantaneous growth rate and temperature, and the unexplained variations in DOC in the summer experiments suggest that some process is operating beyond the control of this experimental design. A strong correlation between net growth and carbon loss in
February indicates that net growth was primarily controlled by bacteria consumption of dissolved carbon. Other processes control the transformations between different pools of carbon in June that lead to the observed increases in DOC. For example, increased abiotic degradation of organic material in summer may reduce DOC consumption by bacteria to limit net growth, and thus growth rates, at higher temperatures.

There was a marginally significant interaction between substrate type and sample collection location. The net growth of dissolved and deposited sediment organic material did not differ between locations. As with the interaction between substrate and sample date, the interaction between substrate and location was caused by a difference that was observed in the net growth of suspended sediment organic material. Net growth was higher on substrates collected from the coastal location than the inland location. The instantaneous growth rate was higher for all sediment organic substrates (both deposited and suspended) collected from the coastal location as well. The initial DOC and bacteria concentrations shown in Figs. 3.2 and 3.3 suggest that the bacteria in experiments using SOM from the inland station were limited by high initial bacteria abundance and low initial levels of organic carbon. Bacteria used a high percentage of the available organic carbon and grew little compared to coastal samples. Perhaps bacteria at the inland station are more selective in their consumption because DOC concentrations are generally higher than those observed at the coastal station (Table 3.1, Chapter 4).

There are differences in both the amount (Fig. 3.4) and the type of organic material available to bacterial consumers in different months. The population of
bacteria consuming organic material changes from month to month as well. Most of these factors were not analyzed in this study, because the primary objective was to compare utilization of the available substrate by local consumers. However, these differences in organic material composition of the bacteria community may contribute to the variations in uptake characteristics observed on different sampling dates and at different estuarine locations.

Conclusions

The results of these experiments demonstrate that organic material removed from suspended and deposited sediment is proportionately more labile than dissolved organic material from the same location. In the February experiments that showed a correlation between bacteria and carbon changes, between 40% and 100% of the sedimentary organic material was consumed by bacteria, while only 11% of dissolved organic material was consumed. However, the dissolved organic material provides a larger source of organic material for bacteria because the percentage that is labile was more concentrated in estuarine water e.g., ~0.3-4.0 mg OC L\(^{-1}\). The sedimentary organic material that was available to water column consumers was ~0.01-0.02 mg OC L\(^{-1}\). In addition to having a high degree of lability, the organic material from suspended sediment is more efficiently converted to biomass from carbon than other substrates. These indications that sedimentary organic material derived from suspended sediment is efficiently used by bacteria support the idea that adsorption to mineral grains protects organic molecules. However, this protection may not last long in an estuarine environment, where much of the sedimentary organic material exchanges readily between water and mineral surfaces. The results of experiments
conducted at different locations and in different months illustrate how much the 
uptake of sedimentary organic material can vary among seasons and spatially. The 
potential uptake of sedimentary organic material by bacteria will be greatest when the 
ambient DOC concentrations are low, particularly if the water is turbid and provides 
many surface sites for temporary organic material storage.
CHAPTER 4
MINERALOGICAL AND ENVIRONMENTAL CONTROLS ON ESTUARINE SEDIMENT ORGANIC CHARACTERISTICS

Introduction

Adsorption of organic molecules to mineral sediment grains may influence the composition and abundance of organic material preserved in deposits and cycled in the water column. Suspended mineral-organic aggregates provide a substrate for enhanced metabolic activity that can influence the type of organic material deposited (Alldredge and Silver, 1988). Organic material preservation in continental shelf deposits has been attributed to protection of molecules adsorbed to mineral surfaces (Mayer, 1994b). Transformations occurring in estuaries are expected to determine whether offshore deposits preserve terrestrial or marine organic material (Lee, 1994b; Lee and Wakeham, 1992).

Estuaries receive organic material from rivers, land or the coastal ocean, and produce it in situ through primary production. The source and degree of degradation of organic material determine its composition and consequently, its reactivity in the environment. Amino acid and protein groups containing nitrogen are easily decomposed and so are consumed relatively quickly leaving remaining organic compounds depleted of nitrogen (Sigleo et al., 1982). This accounts for the difference in C:N ratio between labile, compounds containing high nitrogen content and refractory, compounds containing low nitrogen content (Guo and Santschi, 1997).

Mineral sediment in estuaries consists of fine silt grains and clay minerals. Clay minerals are charged particles that may flocculate when suspended in salt water by suppression of the repulsion between the similar charges on individual clay (van...
Olphen, 1977). This effect is documented better in laboratory simulations than in estuarine water (Eisma, 1986; Gibbs et al., 1989). Mineral grains in natural environments are coated with a ubiquitous layer of organic material that changes its chemical nature and could affect its tendency to flocculate at low salinity (Gibbs, 1983; Hunter and Liss, 1979). The platy shape of clay minerals gives them high specific surface area, which allows them to adsorb high levels of organic material. This characteristic makes them important in the sequestration of organic material in deposits (Keil et al., 1994b).

This research examined the association of minerals with organic material in an estuary. Changes in the amount and C:N ratio of mineral-attached organic material were documented along the salinity gradient and related to variations in estuarine water quality, and sediment mineralogy and surface area. Suspended sediment aggregates collected along the gradient were described and used with sediment organic characteristics to examine the role of suspended sediment in transporting labile organic material throughout the estuary.

Methods

Study area

Barataria Bay, in southeast Louisiana, U.S.A., is a shallow (<2 m deep) interdistributary basin west of the Mississippi River (Fig. 4.1). The watershed is in a temperate climate and supports agricultural fields, cypress-tupelo swamp, and fresh, brackish and saline marshes. Sediment is imported to the estuary by drainage of these environments and from the continental shelf of the Gulf of Mexico. Sediment is also
redistributed within the estuary by resuspension and lateral transport during the passage of seasonal storm fronts.

Figure 4.1. Map of Barataria Bay showing locations where sediment and water were sampled for the analyses described in this paper. Sample locations are marked by their station numbers.

Scanning electron microscopy

Samples collected in May 1995 from stations 9, 16, 23 and 30 were prepared to examine suspended sediment aggregates using scanning electron microscopy. A 90 mL sample was collected from the surface water in a small plastic bottle with as little
disturbance as possible, and preserved by adding 10 mL of 25% glutaraldehyde. Samples were stored on ice and refrigerated upon return to the laboratory.

Approximately 5 mL of each sample was filtered onto a 25 mm polycarbonate membrane filter of 0.46 μm pore size using a vacuum. Samples were dehydrated in baths of successively higher concentrations of ethanol in distilled water (25%, 50%, 75%, 87%, 95% and 100%). Each ethanol bath lasted 10 minutes, and the final one was repeated to ensure complete dehydration. Filters were critical point-dried using carbon dioxide and then fixed to scanning electron microscope stubs with double-sided tape. These samples were gold-coated and secondary electron images were examined using a JEOL JSM-840A scanning electron microscope.

**Water quality**

Samples were collected at various stations along the estuarine salinity gradient in Barataria Bay, Louisiana in January, March, April and August 1998. Surface water (500 mL) was collected at each location, stored on ice and returned to the laboratory for water quality analyses. The salinity was measured in the laboratory using a conductivity meter. Total suspended sediment concentration was determined by drying rinsed, filtered samples (Whatman GF/C, mesh diameter 1.2 μm) at 60°C for 24 h. Filtered water samples (Whatman GF/F, mesh diameter 0.7 μm) were analyzed for dissolved organic carbon (DOC) concentration on a Shimadzu TOC 5000A analyzer by platinum catalyzed oxidation at 570°C. Particulate organic carbon (POC) was measured as the difference between carbon analyses on raw and filtered samples. Plankton containing chlorophyll $a$ were concentrated from a volume of water by low-vacuum filtration through glass fiber filters. The pigments were extracted using a
solution of 90% acetone and 10% dimethyl sulfoxide (DMSO), and their fluorescence measured after centrifugation. Fluorescence readings were used to calculate the concentration (in µg L⁻¹) of chlorophyll Α in the sample extract (Arar and Collins, 1992).

**Sediment physical characteristics**

Sediment from the deposit was collected using an Eckman dredge. Surface water (~80 L) was sampled with a bucket. The bottom sediment was collected on each date, stored in bags on ice and refrigerated upon return to the lab. Surface water was collected in November, March and April, and refrigerated in the laboratory, allowing sediment to settle for 24 hr. After the overlying water was siphoned off, remaining water and sediment were centrifuged to remove water and concentrate sediment. Part of each sediment sample was dried at 60°C, ground for specific surface area and organic analysis, while a second part was left wet to prepare samples for X-ray diffraction.

Dried sediment collected in November 1997 was oxidized using hydrogen peroxide to remove organic material and ground to disaggregate the sample. Specific surface area (SSA) was measured using the one-point BET (Brunauer-Emmett-Teller) method and the N₂ adsorption isotherm (Mayer, 1994b).

Wet sediment collected in April 1998 was dispersed in 0.2 wt. % Na₂PO₄ solution. The sediment was agitated to suspend the sample, and a representative sample of the clay fraction (<2 µm) was withdrawn after sand and silt fractions had settled. This process was repeated twice and the clay sample centrifuged to remove Na₂PO₄ solution. The samples were saturated with K from a 0.1 N KCl solution and

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excess chloride removed by rinsing until no precipitation was observed after adding AgNO₃. For each type of sediment, an oriented smear was prepared (Moore and Reynolds, 1989). The slide was analyzed after air-drying, saturation in ethylene glycol, heating at 300°C and heating at 550°C. A second slide was prepared after solvating the sample with liquid glycerol. This slide was analyzed after air-drying, heating to 300°C and heating to 550°C. Diffraction patterns were generated on a Siemens D5000 X-ray diffractometer using 1.5406 Cu radiation.

Relative quantities of different minerals in each sample were compared using a numerical scheme that produces a quantitative representation of the mineral abundance rather than a true estimate of weight percentage (Hughes et al., 1994). The method suggests using peaks located at >10°2θ to minimize intensity errors related to differences in preferred orientation (Hughes et al., 1994; Moore and Reynolds, 1989). In this case first order peaks (001) located at <10°2θ were used instead, because the intensities of the higher angle peaks were so low. The peak height used for each mineral was corrected by subtracting background contributions. Smectite, illite and kaolinite peaks were measured on the diffraction pattern of the glycerol solvated sample. The chlorite peak was difficult to distinguish on these diffractograms, so it was measured after the sample was heated to 550°C. The intensities from the two patterns were standardized by comparing with the measured quartz peak intensity at 20.8°2θ.

**Sediment organic characteristics**

Bottom sediment from November, January, March, April and August and suspended sediment from November, March and April were analyzed for carbon and...
nitrogen content. Samples were collected, dried and ground as described above.
Inorganic carbon was removed with concentrated HCl vapor (Stern and Hedges, 1984), so that the measure would include only organic carbon content. Organic carbon and total nitrogen were analyzed using a Perkin Elmer CHNS/O model 2400 analyzer. A saturated solution of CsCl (\( \rho = 1.9 \text{ g cm}^{-3} \)) was used to separate unattached organic material from mineral grains in several samples. The dry weight of unattached organic material accounted for <3% of the sediment weight. The results reported here used samples that were not treated to remove unattached particulate organic material, because the treatment adds salt and the extra steps required to remove the salt alter the organic content of the sample. The variation in organic composition among untreated samples was assumed to represent that of attached organic material.

**Data analysis**

Linear relationships between pairs of variables were examined by constructing a correlation table that included all data collected in 1998, including: distance of sample station from the Gulf of Mexico, water quality (salinity, chlorophyll \( a \), suspended sediment concentration, dissolved organic carbon concentration, particulate organic carbon concentration), suspended and deposited sediment organic characteristics (organic carbon, total nitrogen, carbon to nitrogen ratio) and clay mineral indexes. Pearson's correlation coefficients and significance levels were calculated using SAS statistical software (SAS Institute, 1996). Specific surface area was not included in this correlation matrix. It was compared to sediment organic characteristics using simple linear regression.
Results

Scanning electron microscopy

Individual particles observed by SEM ranged in length from \(<1 \mu m\) to \(>50 \mu m\), and included individual sediment grains, sediment aggregates, bacteria and other organisms (Fig 4.2a-d). Suspended sediment aggregates were composed of mineral flakes, organic coatings and biogenic particles, including individual diatoms and bacteria. Despite treating samples as gently as possible, sediment aggregates appeared somewhat flattened against the filters on which they were mounted, indicating that some aggregates collapsed during sample collection and preparation.

The aggregates that withstood treatment varied in abundance, size, shape and composition along the salinity gradient. The downstream station is 15 km from the Gulf of Mexico, and had a salinity of 4.7 psu on the date of collection. This water sample contained few sediment aggregates, which were small (\(~5 \mu m\) in length) and composed primarily of mineral particles. The largest one observed (Fig.4.2a) was a narrow, branched structure less than 10 \(\mu m\) wide and 35 \(\mu m\) long. Samples collected 41 km upstream in 0.6 psu salinity contained more aggregates, which were of intermediate size (10-15 \(\mu m\) long). Most consisted of mineral grains held together in unbranched structures (Fig. 4.2b) that appeared more durable than the aggregate observed downstream (Fig. 4.2a). Further upstream (70 km) in fresh water, the aggregates were nearly somewhat larger (15-20 \(\mu m\) long), and showed an increase in the presence of organic material. The aggregate shown in Fig. 4.2c is relatively small, only \(~5 \mu m\) long, and has numerous strands of organic mucous similar to other aggregates observed at this station and upstream. Aggregates collected \(~100 km\)
Figure 4.2. Scanning electron micrographs of suspended sediment aggregates collected in May 1995 in Barataria Bay. A) Collected 15 km upstream from the mouth of the estuary; salinity = 4.7 ppt. B) Collected 41 km upstream; salinity = 0.6 ppt. C) Collected 70 km upstream at salinity = 1 ppt. Arrows show filaments of organic mucous. D) Collected 100 km upstream in freshwater. Arrows show two different species of diatom.
upstream in freshwater were the largest aggregates observed (routinely >20 μm long). A well-developed mucous coating obscured mineral edges on the largest aggregate observed that was 20 μm wide and ~100 μm long (Fig. 4.2d). These aggregates also contained numerous biogenic particles; several types of diatom are incorporated into the aggregate in Fig. 4.2d.

The aggregates are similar in size and morphology to those observed elsewhere (Pierce, 1991; Syvitski, 1991). They are smaller than marine snow aggregates (~15 mm long) observed in situ, indicating that sampling procedures did not preserve all aggregates (Syvitski, 1991; Wells, 1989). Changes observed along the salinity gradient are not consistent with observations of Pierce (1991). He documented large, primarily mineral aggregates in freshwater that he attributed to salinity flocculation at very low ionic concentrations, and noticed an increase in the organic contribution to aggregation in brackish and marine water. The aggregates observed here show no evidence of salinity induced flocculation. The upstream decrease in salinity coincides with an increase in the abundance of organic material in freshwater aggregates. Freshwater aggregates appear more robust, and they contain organic binders that may increase their chances of withstanding disruption during sampling. The increase in salinity may limit the occurrence of organic material binders in aggregates (Eisma, 1986), or the amount of organic material available to the aggregates may change upstream. Either way, the organic component of aggregates controls the differences observed in these estuarine sediment aggregates.
Water quality

The mean and standard deviation of water quality characteristics are shown in Table 4.1. The salinity at stations where samples were collected ranges from 0 psu to 23.5 psu. The mean is low and has a large standard deviation, 3.9 ± 6.8 psu, because collection locations were chosen to allow the observation of changes that occur in the low salinity zone. The salinity gradient fluctuates rapidly near the Gulf of Mexico, resulting in large error bars for the two downstream stations salinity ranges from 6.2 psu to 23.5 psu (Fig. 4.3a). The error bars are smaller upstream, because salinity remains below 1 psu at 55 km, and near 0 psu at 100 km from the Gulf of Mexico. The highly significant negative correlation between salinity and distance upstream is expected because of estuarine mixing of fresh and marine waters (Table 4.2).

Total suspended sediment (TSS) averaged 46.2 ± 34.1 mg L\(^{-1}\) in Barataria Bay (Table 4.1). Highest values were observed in April, and lowest values were observed in August. Variation among samples did not correspond to distance along the gradient (Fig. 4.3b). Both the highest (160 mg L\(^{-1}\), April) and the lowest (7 mg L\(^{-1}\), August) suspended sediment concentrations were observed at Little Lake, located ~41 km from the Gulf.

Dissolved organic carbon (DOC) concentrations averaged 10.6 ± 2.52 mg L\(^{-1}\) in Barataria Bay (Table 4.1). The highest DOC values were observed in January, and the lowest values were observed in August. The DOC increases from low values at the Gulf of Mexico to a plateau (or minor decrease) in the middle estuary (Fig. 4.3c). The concentration of DOC increases again ~100 km upstream to the maximum observed values (averaging ~15 mg L\(^{-1}\)) at 110-125 km from the Gulf of Mexico. The
DOC concentration is positively correlated with distance upstream and negatively correlated with salinity (Table 4.2).

Particulate organic carbon (POC) averaged $3.2 \pm 3.0 \text{ mg L}^{-1}$, with high values in the middle part of the estuary and lower values occurring both upstream and downstream (Table 4.1, Fig. 4.3d). High values were observed in August while low values occurred in January. Although both show similar minimum values of POC

Table 4.1. Mean and standard error of water quality and sediment characteristics measured in Barataria Bay, 1997 and 1998. Values for suspended sediment are calculated separately from values for deposited sediment. TSS is total suspended sediment; DOC is dissolved organic carbon; POC is particulate organic carbon; Chl a is chlorophyll a. The number in parenthesis gives the corrected smectite index after removing an outlier.

<table>
<thead>
<tr>
<th>Water quality</th>
<th>mean</th>
<th>SD</th>
<th>Sediment characteristics</th>
<th>Deposit</th>
<th>Suspension</th>
</tr>
</thead>
<tbody>
<tr>
<td>salinity (psu)</td>
<td>3.86</td>
<td>6.77</td>
<td>Surface area m$^2$ (g sediment)$^{-1}$</td>
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<td>TSS (mg L$^{-1}$)</td>
<td>46.23</td>
<td>34.12</td>
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<td>55</td>
<td>3.4</td>
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<td>DOC (mg L$^{-1}$)</td>
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<td>2.52</td>
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</tr>
<tr>
<td>POC (mg L$^{-1}$)</td>
<td>3.22</td>
<td>3.03</td>
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<td>Chl a ((\mu)g L$^{-1}$)</td>
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<td>44.88</td>
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<tr>
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<td>8.22</td>
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<td>C:Nat</td>
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Table 4.2. Pearson correlation coefficients and significance levels for each pair of variables whose correlation was significant at the 0.05 level. There are no significant correlations between deposited and suspended sediment characteristics. The number of samples is given (as 'n') in column and row headings.

<table>
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<th>Salinity</th>
<th>Chlorophyll a</th>
<th>TSS</th>
<th>DOC</th>
<th>POC</th>
<th>OC</th>
<th>TN</th>
<th>CN</th>
<th>Sme</th>
<th>Ill</th>
<th>Kao</th>
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<td>0.042</td>
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<td>0.0012</td>
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<td>Smectite n=6</td>
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<tr>
<td>Illite n=6</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinite n=6</td>
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<td></td>
<td>0.021</td>
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<th>TSS</th>
<th>DOC</th>
<th>POC</th>
<th>OC</th>
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<tr>
<td>Smectite n=6</td>
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<tr>
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<td>Kaolinite n=6</td>
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<td></td>
<td>0.032</td>
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Figure 4.3. Water quality characteristics averaged over four sampling dates (January, March, April and August 1998). Error bar is 1 standard deviation.
concentration (0.0-0.2 mg L\(^{-1}\)), the maximum values observed in this estuary (10.2 mg L\(^{-1}\)) are higher than those observed for Lake Pontchartrain (4.2 mg L\(^{-1}\)), which has similar turbidity conditions (Bianchi and Argyrou, 1997). The POC concentration varies inversely with DOC (Table 4.2).

Chlorophyll \(a\) concentrations averaged 29.6 ± 44.9 \(\mu\)g L\(^{-1}\) with high values occurring upstream and low values occurring closer to the coast (Tables 4.1, and 4.2, Fig. 4.3e). High values observed here (205 \(\mu\)g L\(^{-1}\)) exceed those reported by Bianchi (1997) for Lake Pontchartrain (6.9 \(\mu\)g L\(^{-1}\)), reflecting the nutrient enrichment that has been documented in inland portions of Barataria (Rabalais et al., 1995).

**Specific surface area**

Specific surface area is higher in suspended sediment, with an average of 55.0 ± 6.9 m\(^2\) g\(^{-1}\), than in deposited sediment, which has an average surface area of 28.5 ± 6.9 m\(^2\) g\(^{-1}\) (Table 4.1, Fig. 4.4). The difference between suspended and deposited sediment probably reflects the control of grain size on sediment surface area.

![Figure 4.4. Specific surface area of suspended and deposited sediment collected in November 1997.](image)
Sediment that has high surface area is finer-grained and tends to remain in suspension longer. Sediment with lower surface area is coarser and more likely to be found in the sediment deposit. Sediment collected at three interior stations shows minimal variation in surface area of sediment from both environments. In contrast, suspended sediment from the mouth of Barataria Bay has the highest surface area (60 m$^2$ g$^{-1}$), while the deposited sediment from this station has the lowest surface area (18.9 m$^2$ g$^{-1}$).

**Clay mineralogy**

Suspended and deposited sediments include quartz and the clay minerals smectite, illite, kaolinite and chlorite, as indicated on the diffractograms of a typical sediment (Fig. 4.5). This mineral assemblage has been documented in coastal and shelf deposits of the Mississippi Delta (Johns and Grim, 1958; Stewart and Patrick, 1990; Taggart and Kaiser, 1960). The composition of clay does not appear to vary consistently along the salinity gradient (Fig. 4.6), however, there are several notable differences between suspended and deposited sediments.

Diffractograms for suspended sediment had lower intensity than those of deposited sediment. Organic material associated with the sediment probably reduced the intensity of the diffraction patterns by interfering with the clay mineral peaks. Suspended material contains more organic material than deposited material, and was more affected by the interference, so the suspended sediment clay peaks were lower in intensity than those of deposited sediment.

Another difference between suspended and deposited sediment is the proportion of clay minerals each contained. The average suspended sediment contained smectite, illite, kaolinite and chlorite in the proportion 41:30:29:8 while the
proportions in deposited sediment were 45:37:32:10 (Table 4.1). The smectite index for deposited sediment is high, which may be a consequence of navigational dredging at that station. Eliminating that data point gives a smectite index of 4.0 for deposited sediment. To compare the relative abundance of each mineral in the suspension and

![XRD patterns showing the effects each treatment on potassium saturated sediment.](image)

Figure 4.5. Representative XRD patterns showing the effects each treatment on potassium saturated sediment. The sample is suspended sediment collected April 1998 at station 8 (13 km upstream from the mouth of the bay).

the deposit, each deposited sediment mineral index was divided by the corresponding index for suspended sediment. Numbers greater than one in this ratio indicate the mineral is more abundant in the deposit than in the suspension, while numbers below one indicate the mineral is less abundant in the deposit than in the suspension. The
ratio is 0.98 (smectite): 1.22 (illite): 1.10 (kaolinite): 1.25 (chlorite). Deposited sediment is richer in chlorite, illite and kaolinite than the suspension, while the suspension is enriched in smectite with respect to the deposit.

Figure 4.6. Ratio of the maximum peak height of each clay mineral to the quartz peak maximum height. Peak heights for smectite (crosses), illite (closed circles) and kaolinite (squares) were taken from diffractograms of glycerol solvated samples. Chlorite peaks coincide with those of other minerals on this treatment, so the chlorite peak height was taken from the diffractogram of a sample heated to 550°C that isolated the chlorite peak. The open circles represent chlorite.

Diffraction patterns of glycerol-saturated sediment from three stations illustrate the variation in smectite and chlorite concentrations in the deposit and suspension (Fig. 4.7). Smectite and chlorite peaks overlap broadly near 14-15 in air-dried

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sediment. Saturating the sediment with glycerol expands smectite particles to their maximum spacing (18°), while chlorite spacing remains at 14°. The chlorite and smectite peaks have been separated in Fig. 4.6 to show a higher smectite peak at 18° and a lower chlorite peak at 14° in suspended sediment, resulting from relative enrichment of smectite in the suspension. The high and low peak positions are reversed in deposited sediment showing relative enrichment of chlorite in the deposit.

Figure 4.7. XRD patterns for glycerol-solvated sediments from each station collected in April, 1998. The number to the right of each pattern indicates the station where the sediment was collected.

There are several significant correlations that involve clay mineral indexes (Table 4.2). The correlations shown between salinity and smectite in suspension and kaolinite in the deposit are not actually significant because both are influenced by an

97
outlier at high salinity. In both suspended and deposited sediments, the kaolinite index is related to the illite index. The indexes of illite and kaolinite in suspension are positively correlated to the concentration of sediment in suspension (Figure 4.8). The smectite index does not show the same trend with increased suspended sediment concentration. The three samples with highest smectite abundance were collected kaolinite, smectite is likely to remain longer in suspension after waves dissipate.

![Figure 4.8. Variation of clay mineral content as a function of TSS (total suspended sediment concentration). The stations where the sediment was collected and where these sediment concentrations were observed are labeled above the points.](image)

Illite:
\[ y = 0.016x + 1.94 \]
\[ R^2 = 0.96 \]
Kaolinite:
\[ y = 0.015x + 1.84 \]
\[ R^2 = 0.78 \]
Sediment organic content

Organic carbon (OC) composes between $8.2 \pm 1.7$ wt. % in suspended sediment and just over half that, $4.3 \pm 2.5$ wt. %, in deposited sediment (Table 4.1). Suspended sediment varies little with distance along the transect while deposited sediment shows a small increase in OC in upstream locations (Fig. 4.9a). Total nitrogen (TN) averages in $0.87 \pm 0.23$ wt. % in suspended sediment and less than half

![Graphs showing organic carbon, total nitrogen, and ratio of carbon to nitrogen]

Figure 4.9. Organic characteristics of suspended (open circle) and deposited sediment (closed circle). a) Percent organic carbon; b) percent nitrogen and c) ratio of carbon to nitrogen averaged for samples collected in January (deposit only), March (deposit and suspension), April (deposit and suspension), and August (deposit only) of 1998.
of that, 0.40 ± 0.28 wt. %, in deposited sediments. Both deposited and suspended sediments increase in TN with distance upstream, and deposited sediment shows greater variation (Fig. 4.9b).

The carbon to nitrogen ratio (C:N) averages 11.3 ± 2.2 in suspended sediment and slightly higher, 13.5 ± 3.9, in deposited sediment. This quantity decreases upstream in both deposited and suspended sediments, and similar to both OC and TN the deposited sediment has greater variation than suspended sediment (Fig. 4.9c).

All three indicators of organic content (OC, TN and C:N) are related to the specific surface area (Fig. 4.10). The OC content of sediment increases with increases

![Graph showing the relationship between specific surface area and percent organic carbon and nitrogen content.](image)

**Figure 4.10.** a) Percent organic carbon (open circles= suspension, crosses=deposit) and nitrogen (open squares=suspension, closed squares=deposit) as a function of specific surface area (m² g⁻¹). The line represents the relationship for delatic sediment in Mayer (1994). b) Organic carbon to nitrogen ratio as a function of specific surface area for suspended and deposited sediment.
shelf sediments. Carbon content falls closer to the relationship Mayer (1994) documented for deltaic sediments (Fig. 4.10). Points for sediment from the deposit fall close to Mayer's line, but suspended sediment appears to decrease in OC for increased surface area. Sediment TN concentration also has a positive linear relationship to surface area. The slope of this relationship is lower than that of OC. The C:N ratio varies inversely with specific surface area (Fig. 4.10b).

The organic characteristics of sediment were significantly correlated to several other water quality and sediment variables. They are grouped by organic variable in Figs. 4.11-14. Organic carbon in deposited sediment varies as a function of distance upstream (Fig. 4.11a), but the relationship explains only ~44% of the variability in the OC of deposited sediment. Organic carbon in suspended sediment is related to the

![Figure 4.11](image.png)  
**Figure 4.11.** Factors controlling variation of organic carbon in estuarine sediment. a) Organic carbon as a function of collection location (km upstream from mouth of bay) in deposited (1,3,4,8-98; crosses) and suspended sediment (3,4-98; circles). b) Organic carbon as a function of smectite content in suspended sediment (4-98).
smectite index (Fig. 4.11b), with ~91% of variation explained by the smectite index. The distance upstream of sampling locations is a significant factor in the variation of TN in both suspended and deposited sediment (Fig. 4.12a), but as with OC the relationship leaves much of the variation unexplained. There is a highly significant relationship between chlorophyll $a$ and TN in suspended sediment ($R=0.88$, significance = 0.0002, Fig. 4.12b). Similar to OC and TN, the C:N ratio in deposited sediment is related to distance upstream, however C:N decreases upstream (Fig. 4.13a). In suspended sediment, C:N is related to the concentration of sediment in suspension (Fig. 4.13b). In both suspended and deposited sediment, C:N is negatively correlated with TN (Table 4.2). Similarly, TN is strongly related to OC (Fig. 4.14).

Figure 4.12. Factors controlling variation of organic carbon in estuarine sediment. a) Total nitrogen as a function of collection location (km upstream from mouth of bay) in deposited (1,3,4,8-98; crosses) and suspended sediment (3,4-98; open circles). b) Total nitrogen as a function of smectite content in suspended sediment (4-98).
Figure 4.13. Factors controlling variation of C:N ratio in estuarine sediment. a) The C:N ratio as a function of collection location (km upstream from mouth of bay) in deposited (1-3, 8-98, crosses) and suspended sediment (3, 4-98; circles). The C:N ratio as a function of smectite content in suspended sediment (4-98).

Figure 4.14. Relationship between total nitrogen and organic carbon of sediment. Nitrogen content of sediment groups into two sets of values: deposited sediments from most of the transect (0-90 and 110-125 km upstream) and suspended sediments with deposited sediment collected 92-110 km upstream from the mouth of the bay).
Discussion

Variation in sediment organic characteristics

In suspended sediment the controls on each organic component seem independent because OC, TN and C:N are correlated to different variables. Organic carbon depends primarily on surface area, while TN depends on chlorophyll $a$ and location, and the C:N ratio depends on concentrations of suspended sediment. In deposited sediment all organic variables correlate only to distance and surface area. Even so, the correlations are of variable strength, indicating that different factors contribute to the variation of each organic component. Emphasis is usually placed on organic carbon as an indicator of sedimentary organic carbon, because carbon is the main constituent in sedimentary organic material. However, the differences in correlations reflect differences in composition of sediment organic material.

The nitrogen content of sediment is generally closely related to the carbon content, but the relationship is strongest for several subsets of the data (Fig. 4.14). Deposited sediment collected in most of the estuary shows a strong linear increase in nitrogen with organic carbon content. Suspended sediment tends to have higher carbon content than these deposited samples; even when its carbon content lies within the range defined by deposited sediment, suspended sediments are relatively enriched in nitrogen. Deposited sediment collected 90-110 km from the mouth of the estuary appears similar to suspended sediment in its organic loading, which indicates a relative enrichment of nitrogen over sediment deposited in other parts of the Bay.

The C:N ratio of organic material indicates that changes in the relative amounts of either element affect the freshness or biological availability of the organic...
material. Samples that are high in nitrogen may include amino acids or other easily utilized organic groups (Sigleo et al., 1982). By contrast, when the C:N ratio is high, the organic material may be depleted of these groups, leaving relatively old, degraded compounds. In sediment deposits variation in the C:N ratio of associated organic material has been related to the prevalence of vascular plant detritus in sands and the presence of terrestrial soil nitrogen in clay sediments (Keil et al., 1994b). In Barataria Bay C:N varies from 7.9 to 25.1 (Fig. 4.9). The maximum value is slightly lower than the high of 30.6 reported in Lake Pontchartrain (Bianchi and Argyrou, 1997), perhaps indicating an increased incidence of estuarine production in parts of Barataria Bay.

Physical controls on sediment organic characteristics

Both surface area and clay mineral content influence the organic composition of estuarine sediments. The surface area strongly controls the amount of organic carbon and total nitrogen on sediments, as well as the C:N ratio (Fig. 4.10). The positive linear relationship between organic carbon and surface area was documented by Mayer (1994b). Like organic carbon, the total nitrogen content of sediment also varies directly with surface area. In contrast, the C:N ratio decreases with increasing surface area, indicating that changes in nitrogen control the variation in this relationship. Keil et al. (1994) documented similar trends between sediment surface area and both nitrogen and the C:N ratio. There was also a significant correlation between the organic carbon content of suspended sediment and the clay mineral index for smectite (Fig. 4.11b and Table 4.1). Deposited sediments showed no obvious relationship between carbon and smectite content, although Keil et al. (1994) showed strong correlation between these variables.
It is expected that clay mineralogy will influence sedimentary organic carbon concentrations, because it controls the surface area of sediment. Of the clay minerals present in these samples, smectite has the highest total surface area, followed by illite, kaolinite and chlorite. Most of the surface area in smectite, and some of the surface area in illite, is interlamellar area that is not available for OM adsorption (van Olphen and Fripiat, 1979). Still, smectite has highest external surface area available for organic adsorption, ~50 m² g⁻¹, followed by illite, ~25 m² g⁻¹, and kaolinite and chlorite, ~15 m² g⁻¹ (van Olphen and Fripiat, 1979). Samples high in smectite have high surface area and should adsorb more organic material than other clay minerals.

The relationship between the amount of a single clay mineral, such as smectite, and the corresponding organic content in sediment is not precise. The surface area of bulk sediment depends on the surface area of each constituent clay and its relative proportion in the sediment. The surface area of each constituent clay depends on the size of the particles. The clay content indexes given here are not direct proportions of the different clay minerals in each sample, which limits the amount of correlation expected between smectite and the organic parameters. Keil et al. (1994) determined specific percentages of clay minerals, and performed each analysis on different size fractions to constrain the surface area and the amount of organic material that adsorbs to sediment grains. Undoubtedly these measures contributed to the strong correlation they documented between smectite and carbon, nitrogen and C:N ratios.

The linear relationship between surface area and organic carbon content is well documented for continental shelf sediments. The amount of organic carbon required to cover a sediment grain with a single layer of organic molecules is ~0.5-1.1 mg OC
Continental shelf sediments comprise ~0.8 mg OC m$^{-2}$ of sediment, leading to suggestions that carbon adsorption to mineral grains protects labile organic material from microbial decomposition (Mayer, 1994b). Deltaic and very fine grained continental shelf sediments (<8 μm) are reported to include 0.2-0.3 mg OC m$^{-2}$ (Keil et al., 1994b; Mayer, 1994b). Most of the data for the suspended estuarine sediments described here fall below the line for deltaic sediments. Mayer (1994) attributed the low slope for delta sediments to an excess of sediment surface area over available organic material in these areas of high sediment delivery. This situation would leave less than a monolayer equivalent coating of organic material on sediment grains (Mayer, 1994b).

The amount of organic material adsorbed to sediment is very little compared that unattached in estuarine water (Chapter 3), so it is unlikely that an inadequate supply of organic material limits the coating of sediment.

The interlamellar surface area of smectite is not supposed to be subject to organic material adsorption or BET surface area measurement (Mayer, 1994b). However, 5-15% of the area may be measured (Hedges, 1977; Keil et al., 1994a). Keil assumed that the fine fraction of sediment in his samples was predominantly smectite and corrected it for the amount of measured, but unavailable, surface area. He multiplied the surface area by 0.6, the ratio of the surface areas of kaolinite clay (which has no interlamellar area), and smectite (which has high interlamellar surface area). This correction raised the slope of his carbon to surface area relationship to the level observed for other sediments of 0.8 mg OC/g$^{-1}$ sediment. He concluded that little organic material is associated with the interlamellar area of expandable clay minerals. This explanation encouraged Mayer (1994) to conclude that expandable
clays have no special role to play in carbon preservation. However, this solution assumes that all surface area is associated with smectite. Converting the surface area to what might be expected of kaolinite fails to account for two factors. For one thing, there is a strong relationship between carbon and smectite content. In addition, smectite is higher than kaolinite in external, as well as internal, surface area. Although the correction is not as neat as Keil et al. (1994) presented it, the solution may be acceptable. Mayer (1994) and Keil et al. (1994) both present data showing a decline in the carbon to surface area relationship at high values of surface area. Suspended sediments in Barataria Bay, which have high surface area, also appear to decrease in carbon content with increase in surface area (Fig. 4.10). This trend strongly suggests that not all of the measured surface area of smectite is available to organic adsorption.

Deposited estuarine sediment follows a linear relationship between surface area and organic carbon, but at a lower level of carbon loading than continental shelf sediments (Fig. 4.10). Sediment from the deposit does not relinquish a large amount of its attached organic material during desorption rinses (Chapter 2). Perhaps the level of organic material observed is equivalent to monolayer coverage on surfaces that can adsorb organic molecules. Suspended sediment has lower organic carbon loading per unit of measured surface area, but the organic content is a higher percentage of the sediment's weight. The desorption results show that it is easier to remove organic material from suspended than deposited sediments and that the amount of organic material released by sediment is proportional to the organic content of sediment (Chapter 2). This suggests that suspended sediments carry more than a monolayer of organic material. This is an additional indication that smectite-rich sediment has

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measurable surface area that cannot be used for organic adsorption. The strong
correlations observed between smectite and carbon content in the Keil report and here
contradict Mayer's (1994) conclusion that expandable clays are unimportant in carbon
preservation. They indicate instead that expanding clays are important both to carbon
storage in sediments and to the transport of carbon with suspended sediment.

Water quality and environmental characteristics

Processes that control turbidity determine the quantity and clay mineral
composition of suspended sediment. Illite and kaolinite are both strongly correlated to
suspended sediment concentrations (Fig. 4.8). In addition, smectite content in
sediment is higher in lakes where sediment is susceptible to resuspension than in
channels along the transect. This suggests that suspended sediment preserves a
memory of recent episodes of resuspension in elevated smectite concentrations. The
linear relationship between illite and kaolinite and TSS, and the elevated concentration
of smectite in lake suspensions both point to a hydrodynamic control on suspended
sediment composition that is consistent with the observations of Stewart and Patrick
(Stewart and Patrick, 1990). This relationship indicates an indirect influence of
environmental factors on the organic characteristics of sediment.

The C:N ratio of suspended sediment organic material is also correlated to
TSS, because resuspension introduces nitrogen-depleted sediment organic material
from the deposit into suspension. This means that increases of sediment in suspension
that add suspended SOM available for exchanges do not necessarily contribute more
labile organic material to suspended SOM pools. Exchanges occur continuously; if
sediment remains in suspension long enough, the organic material attached to it will become more like that attached to other suspended sediment.

None of the environmental or water quality variables measured in this study had a significant effect on the organic carbon content of suspended sediment. Most of the variation in this quantity was explained by the smectite index. The total nitrogen in suspended sediment was significantly related to chlorophyll \( a \) concentration in the water as well as the location of the station with respect to the Gulf of Mexico. To evaluate whether the nitrogen in chlorophyll \( a \) controls that associated with sediment, the amounts of nitrogen associated with chlorophyll \( a \) and sediment were compared. Chlorophyll nitrogen was conservatively estimated by assuming a carbon to chlorophyll \( a \) ratio of 30 (Parsons et al., 1984b), and the Redfield carbon to nitrogen ratio of 6.6 (Redfield, 1934). To estimate sedimentary nitrogen the suspended sediment concentration was multiplied by its percentage of nitrogen. In all samples chlorophyll \( a \), which contained an average of \( 1.4 \times 10^{-2} \) mol-N L\(^{-1}\), was at least two orders of magnitude greater than the sedimentary nitrogen, which contained \( 2.0 \times 10^{-5} \) mol-N L\(^{-1}\). From this, it appears that nitrogen associated with biological processes controls the sediment nitrogen. These samples may contain traces of the pigment with phytoplankton cells that settled as sediment, which could skew the nitrogen measurement. Nevertheless, scanning electron micrographs indicate that organic material enrichment does occur upstream, because sediment aggregates are accompanied by thicker layers of adsorbed organic material. This relationship links labile organic compounds to the source of the least weathered organic compounds available in the estuary.
Deposited sediments show significant variation in organic carbon, total nitrogen and C:N ratio with distance from the mouth of Barataria Bay. Amounts of both carbon and nitrogen in sediment increase upstream, while the C:N ratio decreases. None of these constituents is significantly correlated with DOC in overlying water, although DOC increases coincidentally upstream. Concentrations of chlorophyll $a$ also increase upstream along the gradient. In addition, deposited sediment located between 92 and 108 km upstream is enriched in nitrogen, and its C:N ratios are not significantly different from those of suspended sediment. The amount of organic material found on sediment collected in this area is consistently high and suggests that production of organic material exceeds utilization. This correlation indicates that there is an increase in organic storage in the surface sediment upstream. Increased storage may be a consequence of increased nitrogen organic loading to surface sediments in an area of high phytoplankton production. It may also result from a decrease in the occurrence of resuspension upstream. Repeated cycles of resuspension and deposition deplete organic material in deposits (Walsh, 1992). A similar increase in storage upstream was attributed to infrequency of resuspension away from high-energy coastal environments (Oviatt and Nixon, 1975). Low correlation coefficients indicate that factors besides distance upstream contribute to the variation of deposited sediment organic content. Surface area and clay mineralogy do not vary significantly with distance from the mouth of Barataria Bay and probably explain much of the remaining variation.
Summary of organic variation in estuarine sediment

Surface area and clay mineralogy control sediment organic content as shown by their relationship to organic carbon, the dominant constituent of organic material. Environmental and water quality factors have less effect on total organic content of sediment, although the concentration of sediment in suspension determines the mineralogy of suspended sediment. Environmental controls on sedimentary organic material determine its lability. This control is illustrated by correlations between nitrogen and both chlorophyll $\alpha$ and location, and through the correlation between suspended sediment concentration and C:N ratio.

In general, suspended sediment is enriched in organic material, and the organic material on suspended sediment contains more nitrogen, making it more labile. The organic material enrichment on suspended sediment relates directly to an increase in the surface area of suspended sediment over deposited sediment. Deposited sediment is generally depleted of labile organic components, except at stations located ~100 km upstream, where organic material is enriched. Suspended sediment and sediment resuspended from the deposit of this area can be a source of organic material if they are transported from the area of enrichment.

The differences observed in suspended aggregates collected at different locations along the gradient show some of the ways that sediments accommodate the relatively minor increases in carbon and nitrogen content of sediment. The SEM photos refer to samples collected in 1995, while those for C and N analyses were collected several years later. Nevertheless, the variation among aggregates that is observed in the photos is consistent with expectations based on the organic
composition of sediments. These images suggest that sediment suspended in
downstream estuarine waters does not have sufficient organic material to generate the
well-developed aggregates observed upstream. As the amount of organic material
increases, suspended sediments upstream are incorporated into more complicated
aggregates held together by increasing quantities of organic material. The increased
rate of primary production in the enriched area supplements the availability of organic
material required to bind aggregates.

Suspended sediment along the salinity gradient is enriched in organic material
relative to most of the deposited sediment. Sediment leaving the enriched area is
enriched in nitrogen and carbon. As it moves into waters that are depleted of organic
material, organic material exchanges from sediment. Declines in nitrogen content
accompany unchanging organic carbon content in suspended sediment organic
material as sediment moves toward the coast. This indicates that the net exchanges
result in loss of nitrogen, or that nitrogen-rich organic material is consumed
throughout the transport along the salinity gradient. Regardless of whether
consumption occurs while organic material is attached to mineral grains or not, the
transport of suspended sediment is a mechanism that delivers labile organic material
from regions where production is high to less organic-rich locations. During
resuspension, bottom sediment can also be used to transport organic material.
Although deposited sediment retains a low C:N ratio during resuspension, it can
acquire organic material through exchange. Sediment collected during episodes of
extremely high sediment concentration were dominated by resuspended deposited
sediment. However, they released more organic material in desorption experiments than would be expected of bottom sediments (Chapter 2).

The extent to which sediment is transported out of its local environment determines whether exchanges between sediment and the water column can play a role in estuarine organic cycling. By the time sediment leaves the estuary, there is a good chance that it will be depleted of labile constituents, leaving little labile organic material to be preserved in continental shelf sediments. However, some sedimentary organic material collected on the continental shelf is labile and can be consumed by heterotrophic microbes from continental shelf water (Keil et al., 1994a). Perhaps the lability of organic material is relative and depends on what other substrates are available for consumers, and what consumers are present in the environment. Organic material that is considered less labile in an organic-rich estuarine environment may be more desirable to consumers in poorer coastal ocean environments.

Conclusions

The organic characteristics of sediment depend on physical characteristics, primarily specific surface area, and environmental variables, including chlorophyll $a$ concentration and the location of the sediment along the estuarine gradient. The specific surface area of sediment primarily determines the amount of organic material that can be adsorbed. There is a strong relationship between surface area and organic carbon concentrations in deposited estuarine sediment. Although sediment surface area is controlled by clay mineralogy, the size and composition variations of clay limit the degree of correlation between clay indices and organic content. Specifically, suspended sediment organic carbon concentration is strongly related to smectite
content. Organic carbon loading of deposited and suspended sediment per unit surface area is low in estuaries relative to continental shelf sediments, which implies that some of the surface area measured for smectite is not available for organic material adsorption.

The nitrogen content of sediment, an indicator of organic material lability, increases with chlorophyll $a$ concentration and with distance upstream. It is also higher in suspended than deposited sediment, except for sediment deposited in an area ~100 km upstream where labile organic material is stored. Suspended sediment concentration controls both the mineralogy of suspended sediment and the C:N ratio of its associated organic material. These relationships show how environmental factors control the lability of sedimentary organic material.

Changes in suspended sediment organic composition indicate that nitrogen depletion occurs in sedimentary organic material with distance from the enriched area. Suspended sediment transports labile organic material from regions where production exceeds consumption, thereby distributing organic material from potentially polluted areas and providing a source of organic material to areas where it limits estuarine cycling.
CHAPTER 5
CONCLUSIONS

The research described here examined estuarine mineral-organic material attachments to understand how transport through the estuary contributes to changes of the attached organic material, and to evaluate the role of sediment in estuarine organic material cycling. Desorption experiments indicated that organic material exchanges between mineral surfaces and water depend primarily on the initial concentration of organic material on the sediment. Water quality also contributed to this effect. Changes in the salinity of the rinse water used to extract organic material from sediment grains caused variation in dissolved organic carbon concentration and pH. These results suggest that organic material exchanges readily between mineral grains and the estuarine water through which it is transported as it moves downstream.

Highly organic sediment moving through water depleted of organic material could shed organic molecules, but sediment moving through organic rich water will acquire additional organic molecules during its transport. If the organic material can be consumed by heterotrophic bacteria, then organic material exchange between sediment and the water column can provide a mechanism of transporting labile organic material throughout the estuary from regions of high production.

The significance of organic material exchanges in estuarine carbon cycling was examined by determining the lability of sedimentary organic material. Uptake experiments compared the lability of sedimentary and dissolved organic material. All forms of organic material were consumed and incorporated into bacterial biomass. The highest percentage of organic material was consumed in experiments on organic material removed from suspended sediment. This suggests that attachment to
sediment grains offers some protection from degradation to labile organic molecules. Although the protection is probably temporary, it may defer consumption of organic material until the mineral grain to which it is attached has moved from the location where it was produced.

Organic carbon, nitrogen, and the carbon:nitrogen ratio of sediments were examined and related to the location of the sediment along the salinity gradient, as well as water quality factors and sediment physical characteristics. All organic indicators are strongly related to sediment specific surface area, as expected, because a relationship between surface area and organic carbon was shown in continental shelf deposits (Mayer, 1994b). Deposited sediment was low in organic content. Variation in organic content of deposited sediment was related to distance of the collection site from the mouth of the estuary. Suspended sediment had a higher organic content than deposited sediment. Organic carbon content was related to surface area and smectite content of the sediment. Total nitrogen and C:N ratio depended on chlorophyll \(a\) and suspended sediment concentrations, respectively. The different factors contributing to carbon and nitrogen content of sedimentary organic material indicate that while physical factors of sediment control how much organic material adsorbs to sediment, the bioavailability of sediment-attached organic material is a function of water quality.

Organic material exchanges continuously between suspended sediment and water during its transport. Sediment adsorbs thick layers of OM in areas of high production and carries it to OM-depleted areas, where it can be consumed by water column bacteria. The amount of OM introduced depends on suspended sediment concentration, levels of production in the water column, and organic content of
suspended sediment. It is estimated to be 0.2-1.0mg C m$^{-2}$ in Barataria Bay, which equals the daily production of carbon by phytoplankton. By adsorbing labile organic material in productive areas upstream and carrying it downstream where it exchanges from the sediment, suspended sediment distributes OM in estuaries. Consequently, sedimentary organic material represents a significant and previously unrecognized source of carbon to estuarine cycling.
REFERENCES


VITA

Jessica Anne Kastler was born December 17, 1964, in New Orleans, Louisiana, to Arthur McLellan Kastler and Marie Johnson Kastler. She attended Saint Andrews Episcopal Elementary School, Isidore Newman Junior High School and Benjamin Franklin Senior High School before enrolling as an undergraduate at Louisiana State University. An avid reader and indoorsman, she made an uncharacteristic decision late in her freshman year to major in geology. Her future was decided when she became a student worker for the Center for Wetland Resources and started mucking about in the unconsolidated sediments of the Atchafalaya Delta.

After completing her bachelor of science degree in professional geology in 1987, she moved to Ann Arbor, Michigan for graduate studies. After moving to the University of Virginia, she earned her master of science degree in environmental sciences in 1993 by completing a multidisciplinary investigation of patterns of sedimentation on salt marshes on the Eastern Shore of Virginia. Motivated by the offer of a Board of Regents Fellowship, Jessica returned to Louisiana State University for a doctoral program that incorporated descriptive and experimental work to elucidate interactions of mineral grains and organic molecules in Barataria Bay, Louisiana.

Jessica's extracurricular activities in Baton Rouge included literacy tutoring, organic gardening, and her marriage to Andrew Barron, of Scott, Louisiana. She will begin a post-doctoral research position at the Louisiana Universities Marine Consortium in Cocodrie, Louisiana after receiving the degree of Doctor of Philosophy from the Department of Oceanography and Coastal Sciences on May 14, 1999.
Candidate: Jessica Anne Kastler

Major Field: Oceanography and Coastal Sciences

Title of Dissertation: Interactions of Minerals and Organic Materials Along the Salinity Gradient in Barataria Basin, Louisiana

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Jay Cable

J.H. Rabinovitch

Robert P. Randell

Ray E. Turner

Date of Examination: 3/10/99