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Author(s): Gu, Iricanin, Trefry
Subject(s): Indian River Lagoon sediments

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Environmental Chemistry

THE GEOCHEMISTRY OF INTERSTITIAL WATER FOR A SEDIMENT CORE FROM THE INDIAN RIVER LAGOON, FLORIDA

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Department of Oceanography & Ocean Engineering, Florida Institute of Technology, Melbourne, Florida 32901

ABSTRACT: Chemical results for interstitial water from organic-rich sediments in the Indian River Lagoon, Florida, show a classic picture of biogeochemical reactions in anoxic environments. Intertitial nitrate was depleted throughout the sediment column and complete sulfate reduction was observed at a depth of < 9 cm below the seawater-sediment interface. Interstitial water chlorinity decreased sharply with depth suggesting subsurface occurrence or intrusion of groundwater. Ammonia, phosphate and silica concentrations were high showing significant nutrient regeneration. Dissolved sulfide levels were also high and play a primary role in controlling interstitial water metal concentrations.

Estuarine Sediments typically contain >50% water by weight or >70% water by volume. This interstitial water (or pore water) plays an important role as a medium for chemical exchange between sediments and the overlying water. Study of estuarine interstitial water can help assess a number of important environmental concerns including:

1. The redox state (oxic-suboxic-anoxic) in estuarine sediments.
2. Storage of nutrients and potentially toxic species and their release to the overlying water.

1Permanent address: Third Institute of Oceanography, National Bureau of Oceanography, P.O. Box 70, Xiamen, Fujian, People's Republic of China.
3. Reactions which control mineral formation in sediments.
4. The chemical environment in contact with benthic ecosystems.

One of the most interesting and well-studied reactions in estuarine sediments is the oxidation or decomposition of organic matter (Richards and Cline, 1965; Goldhaber et al., 1977). As this decomposition occurs, a variety of products including inorganic nutrients, metals, and inorganic and organic carbon species are released into solution. Microorganisms play a primary role in mediating this process. Under oxic conditions, organic molecules are decomposed in the interstitial water when bacteria use available oxygen (Table 1, Eqn. 1). If organic matter concentrations in the sediment are high, dissolved oxygen may become depleted in the pore water. When this happens, oxidation of organic matter is facilitated by reduction of nitrate, manganese oxides, iron oxides, sulfate, or carbon dioxide as shown in Eqns. 2-6 (Table 1). Froelich and co-workers (1979) note that reactions 2-4 occur in suboxic environments and that reactions 5 and 6 occur under anoxic conditions. Sediment interstitial water thus develops a chemical composition that records the sum of many ongoing reactions.

Dramatic changes in the chemistry of interstitial water can occur as oxic sediments become suboxic or anoxic. The formation of an anoxic sedimentary environment is promoted by large inputs of organic matter. Because estuaries are especially prone to high loadings of nutrients and organic matter, decomposition reactions lead to oxygen depletion in sediments and sometimes in the water column. When oxygen depletion occurs in the water column it may result in hypoxia and fish kills. The Indian River Lagoon, on the east coast of Florida, is typical of many coastal estuaries where nutrient and organic matter loading are producing an environmental stress. This paper provides a preliminary view of chemical reactions in Indian River Lagoon sediments and how interstitial water studies can be applied to these systems.

### Table 1. Interstitial water reactions which lead to the oxidation of sedimentary organic matter.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>((\text{CH}<em>3\text{O})</em>{106}(\text{NH}<em>3)</em>{16}\text{H}_2\text{PO}_4 + 138 \text{O}_2 = 106 \text{CO}_2 + 16 \text{HNO}_3 + \text{H}_2\text{PO}_4 + 122 \text{H}_2\text{O})</td>
</tr>
<tr>
<td>(2)</td>
<td>((\text{CH}<em>3\text{O})</em>{106}(\text{NH}<em>3)</em>{16}\text{H}_2\text{PO}_4 + 94.4 \text{HNO}_3 = 106 \text{CO}_2 + 55.2 \text{N}_2 + \text{H}_2\text{PO}_4 + 177.2 \text{H}_2\text{O})</td>
</tr>
<tr>
<td>(3a)</td>
<td>((\text{CH}<em>3\text{O})</em>{106}(\text{NH}<em>3)</em>{16}\text{H}_2\text{PO}_4 + 236 \text{MnO}_2 + 472 \text{H}^+ = 106 \text{CO}_2 + 8 \text{N}_2 + \text{H}_2\text{PO}_4 + 236 \text{Mn}^{2+} + 366 \text{H}_2\text{O})</td>
</tr>
<tr>
<td>(3b)</td>
<td>((\text{CH}<em>3\text{O})</em>{106}(\text{NH}<em>3)</em>{16}\text{H}_2\text{PO}_4 + 212 \text{MnO}_2 + 424 \text{H}^+ = 106 \text{CO}_2 + 16 \text{NH}_3 + \text{H}_2\text{PO}_4 + 212 \text{Mn}^{2+} + 318 \text{H}_2\text{O})</td>
</tr>
<tr>
<td>(4)</td>
<td>((\text{CH}<em>3\text{O})</em>{106}(\text{NH}<em>3)</em>{16}\text{H}_2\text{PO}_4 + 212 \text{Fe}_2\text{O}_3 \text{(or } 424 \text{FeOOH} \text{)} + 548\text{H}^+ = 106 \text{CO}_2 + 16 \text{NH}_3 + \text{H}_2\text{PO}_4 + 424 \text{Fe}^{2+} + 530 \text{H}_2\text{O} \text{(or } 742 \text{H}_2\text{O}\text{)})</td>
</tr>
<tr>
<td>(5)</td>
<td>((\text{CH}<em>3\text{O})</em>{106}(\text{NH}<em>3)</em>{16}\text{H}_2\text{PO}_4 + 53 \text{SO}_4^{2-} = 106 \text{CO}_2 + 16 \text{NH}_3 + \text{H}_2\text{PO}_4 + 53 \text{S}^{2-} + 106 \text{H}_2\text{O})</td>
</tr>
<tr>
<td>(6)</td>
<td>((\text{CH}<em>3\text{O})</em>{106}(\text{NH}<em>3)</em>{16}\text{H}_2\text{PO}_4 + 53 \text{CO}_2 = 106 \text{CO}_2 + 16 \text{NH}_3 + \text{H}_2\text{PO}_4 + 53 \text{CH}_4)</td>
</tr>
</tbody>
</table>

*After Froelich et al., 1979.*
Study Site—The Indian River Lagoon is a bar-built estuary that extends 200 km along the east coast of Florida. The lagoon has an average water depth of about 1 m with depths of 3 m or greater in the intracoastal waterway where dredging has taken place. Just three inlets connect the lagoon with the Atlantic Ocean. Thus, portions of the system are prone to water stagnation and are susceptible to the cumulative effects of nutrients and other species. Our sampling was carried out in the Eau Gallie River Basin (28° 07.4' N, 80° 37.6' W), located more than 30 km from the nearest inlet and further isolated by its location between two causeways across the lagoon. Previous work suggests that the area has been impacted by anthropogenic inputs (Trefry et al., 1983). Sampling for this study was designed to collect organic-rich sediment now found in many areas of the lagoon. Water depths in the immediate study area are ~0.6-2 m. The salinity of the overlying water at this site ranges from 14-20°/o. Tidal ranges in the Eau Gallie area are <2 cm.

Methods—Sediment was sampled using a stainless steel box corer with dimensions of 50 x 50 x 40 cm. Two subsamples were carefully obtained from the box corer using 7.6-cm diameter plastic tubes.

Interstitial water was obtained by using Teflon squeezers similar to those described by Reeburgh (1967). Samples were processed in a nitrogen-filled glove box and filtered through 0.4 μm pore size Nuclepore filters. Squeezers, filters, and sample bottles were washed with dilute HCl. Interstitial water was obtained from 0.5, 1.0, and 2.0 cm thick sections of the core, with the sample interval increasing downcore. Water samples were stored at 4°C prior to analysis. Eh and pH were measured at selected depths along a separate subsample by inserting the respective probes into the sediment through pre-drilled holes in the plastic liner. These holes were taped during sampling.

Concentrations of sulfide, ammonia, nitrate, nitrile, phosphate, silica, manganese, iron, sulfate and chloride were determined for each sample. Sulfide was measured using the methylene blue method (Fonselius, 1976) combined with potentiometric standardization. Ammonia determinations were made by the sodium hypobromite procedure (Guo and Gu, 1983) and dissolved silica was measured with the silica-molybdate blue technique (Koroleff, 1976). Nitrite, nitrate and phosphate were determined using standard colorimetric methods (Rand et al., 1975). Sulfate concentrations were obtained with the turbidimetric method (Rand et al., 1975). Alkalinity was determined with the pH technique (N.B.O., 1975) which was modified by standardizing the dilute HCl with a borax titration. After aliquots were drawn for the above measurements, the remaining unaltered interstitial water was acidified with 100 μl of concentrated, redistilled HNO₃. Manganese and iron determinations were made by atomic absorption spectrophotometry, using flame and flameless techniques. The analytical precision (coefficient of variation) for this study are as follows: sulfide (5%), sulfate (2%), alkalinity (3%), dissolved silica (3%), ammonia (1%), phosphate (2%), chlorinity (1%) and manganese (1%).

Results and Discussion—The cores obtained from our study site in the Indian River Lagoon were composed of fine-grained, black, organic-rich sediment. During sampling, a strong H₂S odor was detected throughout the core and no burrowing animal tubes were found within the sediment. The processed interstitial water had a slight yellow color suggesting high levels of dissolved organic matter.

In many estuaries, interstitial water chlorinity profiles record seasonal changes in the salinity of the overlying water. For example, in Chesapeake Bay, Matisoff and co-workers (1975) found an annual range of chlorinities in surficial sediment layers of 6-10.5 g/kg. At depths greater than 20 cm, the chlorinity was relatively constant near 10.5 g/kg, except at a shallow water station where chloride concentrations decreased downcore to as low as 2 g/kg. The observed seasonal differences in chloride values for surficial sediments (6-10.5 g/kg) could be related to variations in freshwater runoff to the bay and subsequent exchange between the interstitial and overlying waters.
The one decreasing chloride gradient observed was explained by seepage from a freshwater aquifer (Matisoff et al., 1975).

At our study site in the Indian River Lagoon, interstitial water chlorinity decreased linearly from 10.7-3.5 g/kg over the length of the core (Fig. 1). This decrease suggests that groundwater may be seeping through these sediments from below or that the water table is quite shallow at this location. Tidal pumping is not a significant variable at this location because the tidal range is <2 cm. The chlorinity of lagoonal waters in this area is 8-11 g/kg (Trefry et al., 1983), values consistent with those for near-surface interstitial water. Conservative mixing of estuarine water and freshwater throughout the sediment column is a likely explanation for the observed chlorinity trend downcore. The chlorinity distribution at this site suggests that groundwater may play a role in controlling the salinity of these lagoonal waters.

Interstitial water pH was measured throughout the core and varied only slightly at 7.09 ± 0.06. This value is consistent with calculations by Nissemann and co-workers (1972) which show that a pH of 7.0 should result when the products of marine organic matter decomposition equilibrate in seawater. The redox potential (Eh) was also measured throughout the sediment column and values ranged from a high of -1 mV at 4 cm to -131 mV at 33.5 cm. A sharp drop in potential occurred over the 7-12 cm interval (Fig. 1). In natural water systems, the redox potential is often unstable and thus theoretical interpretation of Eh is difficult (Presley and Trefry, 1980). Nevertheless, a step-by-step chemical reduction sequence is often predicted from the range in potential over which a particular species can or cannot be oxidized (Stumm and Morgan, 1981). Several investigators have reported the disappearance of oxygen at Eh values below about +250 mV, and that nitrate and manganese oxides begin to be chemically reduced (Eqn. 2 and 3) at slightly lower values (in Presley and Trefry, 1980). Iron oxides can be reduced (Eqn. 4) below +100 mV and sulfate reduction occurs at substantially lower values. Matisoff and co-workers (1975) observed a similar Eh profile in Chesapeake Bay to that shown for the Indian River Lagoon (Fig. 1) and found the onset of sulfate reduction occurred along a sharp Eh 0 to -100 mV gradient.

Nitrate and nitrite concentrations were below detection limits (<0.2μM) throughout the sediment column at our Indian River location. This depletion indicates that bacterial decay of organic matter was being carried out under suboxic or anoxic conditions and that the decomposition reaction had already shifted to Eqn. 3b or 4 in the surficial sediments. This condition results from high organic matter inputs to the sediments.

Under reducing conditions, nitrogen is regenerated as N\textsubscript{2} and NH\textsubscript{4}\textsuperscript{+}. At our study site, dissolved ammonia concentrations were found to increase from 1.1 mM at 0.5 cm to 5.3 mM at 39 cm (Fig. 1) with an average of 3.4 ± 1.7 mM. Dissolved ammonia gradients were largest in the top 12 cm where sulfate reduction was most active (Fig. 1). Below 12 cm, complete sulfate reduction had occurred with a concurrent decrease in the ammonia gradient. Ammonia concentrations for our Indian River study site are comparable with
Fig 1. Vertical profiles showing interstitial water concentrations of chloride, silica, ammonia, alkalinity, sulfate, sulfide, theoretical sulfate, manganese, and Eh vs depth in the sediment column.
<table>
<thead>
<tr>
<th>Component</th>
<th>Seawater*</th>
<th>Interstitial Water (Indian River Lagoon)*</th>
<th>Interstitial Water (Chesapeake Bay)*</th>
<th>Interstitial Water (Long Island Sound)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphate (mM)</td>
<td>0.002</td>
<td>0.8 ± 0.1</td>
<td>0.1-0.8</td>
<td>0.01-0.3</td>
</tr>
<tr>
<td>Ammonia (mM)</td>
<td>0.005</td>
<td>3.4 ± 1.7</td>
<td>1-6</td>
<td>0.1-2.7</td>
</tr>
<tr>
<td>Silica (mM)</td>
<td>0.1</td>
<td>1.1 ± 0.2</td>
<td>0.5-0.9</td>
<td>-</td>
</tr>
<tr>
<td>Alkalinity (meq/l)</td>
<td>2.4</td>
<td>18 ± 5</td>
<td>5-40</td>
<td>4-45</td>
</tr>
<tr>
<td>Manganese (µM)</td>
<td>0.01</td>
<td>6 ± 7</td>
<td>400-900</td>
<td>10-300</td>
</tr>
</tbody>
</table>


*This study.

*Matisoff et al., 1975.

*Goldhaber et al., 1977; Aller, 1980.
those measured for the highly reducing sediments of Chesapeake Bay and Long Island Sound (Table 2).

The alkalinity of interstitial water increases as CO₂ is released from decaying organic matter. At our study site, alkalinity increased from 7.8 meq/liter in the top 0.5 cm to 23 meq/liter at 12-14 cm. The average pore water alkalinity for these sediments was 18 ± 5 meq/liter, about 8 times higher than normal seawater, yet comparable with other estuarine interstitial waters (Table 2). At pore water pH, the primary component of the alkalinity is HCO₃⁻.

In the top 6 samples (0-9 cm) the ammonia vs alkalinity relationship is a straight line (r = 0.98) with a slope of 6.1. Following the classic scheme for decomposition of organic matter (Richards and Cline, 1965), the ratio of inorganic carbon to ammonia is 6.6 (Eqn. 4), in reasonable agreement with the results of this study. No increase in alkalinity is observed below 13 cm; however, ammonia concentrations gradually increase downcore. This observation suggests that decomposition of organic matter is still proceeding, but the mechanism has changed. If so, methane generation via reduction of CO₂ (Table 1, Eqn. 6) is the most likely pathway. Methane generation is common in estuarine sediments after sulfate has been appreciably reduced (Kipp and Martens, 1982). Although methane was not measured, the ammonia and alkalinity relationships and the absence of sulfate (Fig. 1) are consistent with the reduction of CO₂ to CH₄, as shown in Eqn. 6.

Accompanying each of the possible reaction pathways for organic matter decomposition is regeneration of inorganic phosphate from organic phosphorus. In the Indian River Lagoon, pore water phosphate concentrations ranged from 0.66-0.97 mM and averaged 0.76 ± 0.12 mM. These values are 10-100 times higher than observed in estuarine waters, but are comparable with values from highly reducing estuarine sediments. Controls on interstitial phosphate concentrations are complex and may result from several reactions which control phosphate release to and removal from the interstitial water, including formation of an iron phosphate phase or adsorption of phosphate on sediment solid phases (Matisoff et al., 1980).

Dissolved silica concentrations in pore water can be enriched by the dissolution of biogenic silica as well as by release of dissolved silica from various silicate minerals. Silica concentrations are influenced by temperature, water composition, pH, sediment composition, and particle size (Fanning and Pilson, 1971; Matisoff et al., 1975). At our study site, dissolved silica values increase sharply in the top 2 cm and continue to increase gradually downcore to 1.4 mM at 39 cm (Fig. 1). The mean dissolved silica value for our core is very high at 1.1 ± 0.2 mM. This value is much higher than commonly found in estuarine waters, somewhat higher than observed in estuarine interstitial water (Table 2), yet lower than the solubility of about 2 mM for amorphous silica.

Decreases in interstitial water sulfate concentrations are a good indicator of reducing conditions in estuarine sediments. The production of hydrogen sulfide during sulfate reduction is one of the more noxious and obvious results
of organic matter decomposition. At our study site, pore water sulfate concentrations decreased from 10.6 mM at the top of the core to essentially zero below 9 cm (Fig. 1). Throughout the core, including the top 1 cm, sulfate concentrations are much lower than those predicted from the $[\text{SO}_4^{2-}/\text{Cl}]$ ratio for normal estuarine waters (0.140). At the top of the core, about one third of the sulfate has been reduced, as shown by comparing the theoretical sulfate profile (for the case where no sulfate reduction has occurred) with the observed sulfate distribution (Fig. 1).

Sulfate reduction leads to sulfide production.Interstitial sulfide concentrations at our study site increase from undetectable levels in the top centimeter to 1.7 mM at 13 cm. The sulfide produced is highly reactive and thus is not a reliable indicator of the extent of sulfate reduction. Sulfide can diffuse from the sediment column as $\text{H}_2\text{S}$ and contribute to the odor so commonly complained about along the Indian River; or it can precipitate in the sediments with metal ions, especially iron. Thus, we note that the moles of sulfate reduced are much higher than the moles of sulfide measured. Diffusion of sulfide downcore or possible influx of groundwater sulfide is evident in Fig. 1 since sulfide levels extend almost 30 cm deeper in the sediment column than the point of zero sulfate.

Metals such as Mn and Fe are usually present in the water column as oxides and hydrous oxides which exist as colloids or as surface coatings on particles (Stumm and Morgan, 1981). Under reducing (suboxic or anoxic) conditions, these metals can be changed to a lower oxidation state and become more soluble. Manganese is especially susceptible to reduction and dissolution in environments such as the organic-rich, reducing sediments at our study site.

In our core, oxygen and nitrate were depleted in the top layers of the sediment and thus manganese oxide was used immediately as an oxidizing agent for organic decay. As a result, a maximum interstitial Mn concentration is reached in the top 0.5 cm with a steep decrease in Mn levels from 16-1 $\mu$M over a 6-7 cm interval. Below 9 cm, a relatively constant but 50 times lower concentration of 0.3 ± 0.1 $\mu$M is observed. These values are all higher than normal seawater, but they are not especially high relative to other estuarine interstitial waters (Table 2). Such lower relative values for Mn in Indian River pore water most likely result from sediment Mn phases present and chemical reactions controlling interstitial Mn concentrations.

As concentrations of the various products of organic matter decomposition increase in the interstitial water, a series of second generation chemical reactions can occur. These reactions sometimes include formation of selected solid phases. Trace metals such as Mn or Fe, which are released to the pore water, may react to form solid phases such as oxides, carbonates, phosphates or sulfides.

The presence of several solid phases has been identified or implied for various estuarine and marine sediments. Bricker and Troup (1975) give evidence for the presence of an iron phosphate phase (vivianite) in Chesapeake
Bay sediments. Similar studies, based on thermodynamic calculations, support the occurrence of a manganese phosphate phase in Lake Erie sediments (Matisoff et al., 1980). A manganese carbonate phase has also been postulated to form in anoxic marine sediments (Pedersen and Price, 1982). In anoxic sediments with high dissolved sulfide loading and higher Mn than Fe concentrations, Mn may precipitate as a manganese sulfide phase (Suess, 1979; Aller, 1980).

In our Indian River Lagoon pore water, Fe concentrations were <0.5 \( \mu \text{M} \). Based on observed high sulfide levels of 0.01-1.7 mM and the solubility product for iron monosulfides, we predict an interstitial water Fe concentration of < 10^{-3} \( \mu \text{M} \). This is certainly consistent with our measured Fe values.

To identify possible controls on interstitial water Mn values, a saturation index (SI) was calculated for three possible Mn phases:

\[
\text{SI} = \log \left( \frac{\text{IAP}}{K_{sp}} \right)
\]

where IAP is the calculated ion activity product for the species of interest and \( K_{sp} \) is the corresponding solubility product. A negative SI value indicates that the pore water is undersaturated with respect to a particular solid phase, whereas a positive value shows oversaturation. The three solid phases considered for Mn, along with their respective \( \log K_{sp} \) values are as follows: MnCO\(_3\), -10.4 (Morgan, 1967); MnS, -17.8 (Aller, 1980); and Mn\(_5\)(PO\(_4\))\(_2\), -34.6 (Nriagu and Dell, 1974). All activity coefficients were corrected for changes in salinity and pH and are as follows: phosphate, 2.46-30.6 x 10^{-4} (Martens et al., 1978); carbonate, 0.053-0.74 (Pytkowicz, 1975); sulfide, 0.11-0.29 (Richards, 1965); and manganese, 0.29-0.40 (Morgan, 1967).

Calculated SI values for our study site (Fig. 2) suggest that the interstitial water is greatly undersaturated with respect to manganese carbonate and phosphate and that these solid phases would not be expected to form. In fact, the SI values for the carbonate and phosphate phases are always less than -1, suggesting that the Indian River Lagoon pore waters are at least 10 times undersaturated with respect to these phases. In contrast, our calculations support the formation of a Mn sulfide phase in the top 2-8 cm of the sediment column where SI values range from -0.2 to 0.5 (Fig. 2). Because the Indian River sediments were rich in sulfide and interstitial Fe concentrations were undetectable, the unusual prediction that manganese levels may be controlled by a sulfide phase is reasonable. It is certainly consistent with the work of Suess (1979) and Aller (1980).

The presence of high dissolved sulfide concentrations in lagoonal pore waters leads to precipitation of metal sulfides and the observed low interstitial water Fe concentrations of <0.5 \( \mu \text{M} \). A similar trend of very low concentrations of elements such as Cd, Cu and Hg in the pore water is also predicted based on similar results by Elderfield et al. (1981) in Narragansett Bay. Thus the probability of metal release from such sediments is low and the sediments are an effective sink.

Previous studies of interstitial water chemistry in the Indian River Lagoon (Carlson et al., 1983; Montgomery et al., 1983) focused on sediments in fring-
Fig. 2. Plot of saturation for manganese phosphate (▲), manganese carbonate (■), and manganese sulfide (●) vs sediment depth. Saturation index (SI) = log [Ion activity product/solubility product].
ing mangroves and grass beds in the Fort Pierce area. In the mangrove and seagrass environments, dissolved ammonia and phosphate concentrations were 8 to >50 times lower than observed in the organic-rich sediments we studied. Interactions among pore water, sediment, and vegetation bring about a somewhat different picture for these mangrove and grass bed sediments than found in the more classic anoxic, non-vegetated sediments of the Eau Gallie basin.

ACKNOWLEDGMENTS—We thank Diane Quinby and Jack Morton for assistance with sampling. Financial support was obtained from the National Oceanic and Atmospheric Administration and The Asia Foundation.

LITERATURE CITED


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ADDENDUM

Outstanding Student Paper Awards, Awardees
Fiftieth Annual Meeting of the Florida Academy of Sciences,
University of Florida, Gainesville—10-12 April 1986

FCREPA—Blair E. Witherington, University of Central Florida, An Analysis of Reproductive Success in the Marine Turtle Nesting Aggregation at Melbourne Beach, Florida


Accepted: June 6, 1986.
Environmental Chemistry

THE GEOCHEMISTRY OF INTERSTITIAL WATER FOR
A SEDIMENT CORE FROM THE INDIAN RIVER
LAGOON, FLORIDA

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Department of Oceanography & Ocean Engineering, Florida Institute of Technology,
Melbourne, Florida 32901

Abstract: Chemical results for interstitial water from organic-rich sediments in the Indian
River Lagoon, Florida, show a classic picture of biogeochemical reactions in anoxic environ-
ments. Interstitial nitrate was depleted throughout the sediment column and complete sulfate
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One of the most interesting and well-studied reactions in estuarine sediments is the oxidation or decomposition of organic matter (Richards and Cline, 1965; Goldhaber et al., 1977). As this decomposition occurs, a variety of products including inorganic nutrients, metals, and inorganic and organic carbon species are released into solution. Microorganisms play a primary role in mediating this process. Under oxic conditions, organic molecules are decomposed in the interstitial water when bacteria use available oxygen (Table 1, Eqn. 1). If organic matter concentrations in the sediment are high, dis-
Table 1. Interstitial water reactions which lead to the oxidation of sedimentary organic matter.

1. \( (\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} \text{H}_3 \text{P} \text{O}_4 + 138 \text{O}_2 = 106 \text{CO}_2 + 16 \text{HN}0_3 + \text{H}_3 \text{P} \text{O}_4 + 122 \text{H}_2 \)

2. \( (\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} \text{H}_3 \text{P} \text{O}_4 + 94.4 \text{HN}0_3 = 106 \text{CO}_2 + 55.2 \text{N}_2 + \text{H}_3 \text{P} \text{O}_4 + 177.2 \text{H}_2 \)

3a. \( (\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} \text{H}_3 \text{P} \text{O}_4 + 236 \text{MnO}_2 + 472 \text{H}^+ = 106 \text{CO}_2 + 8 \text{N}_2 + \text{H}_3 \text{P} \text{O}_4 + 236 \text{Mn}^{2+} + 366 \text{H}_2 \)

3b. \( (\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} \text{H}_3 \text{P} \text{O}_4 + 212 \text{MnO}_2 + 424 \text{H}^+ = 106 \text{CO}_2 + 16 \text{NH}_3 + \text{H}_3 \text{P} \text{O}_4 + 212 \text{Mn}^{2+} + 318 \text{H}_2 \)

4. \( (\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} \text{H}_3 \text{P} \text{O}_4 + 212 \text{Fe}^{2+} (\text{or } 424 \text{FeOOH}) + 848\text{H}^+ = 106 \text{CO}_2 + 16 \text{NH}_3 + \text{H}_3 \text{P} \text{O}_4 + 424 \text{Fe}^{2+} + 530 \text{H}_2 (\text{or } 742 \text{H}_2\text{O}) \)

5. \( (\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} \text{H}_3 \text{P} \text{O}_4 + 53 \text{SO}^- = 106 \text{CO}_2 + 16 \text{NH}_3 + \text{H}_3 \text{P} \text{O}_4 + 53 \text{S}^{2-} + 106 \text{H}_2 \)

6. \( (\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} \text{H}_3 \text{P} \text{O}_4 + 53 \text{CQ}_2 = 106 \text{CQ}_2 + 16 \text{NH}_3 + \text{H}_3 \text{P} \text{Q}_4 + 53 \text{CH}_4 \)

\textit{aAfter Froelich et al., 1979.}

Solved oxygen may become depleted in the pore water. When this happens, oxidation of organic matter is facilitated by reduction of nitrate, manganese oxides, iron oxides, sulfate, or carbon dioxide as shown in Eqns. 2-6 (Table 1). Froelich and co-workers (1979) note that reactions 2-4 occur in suboxic environments and that reactions 5 and 6 occur under anoxic conditions. Sediment
interstitial water thus develops a chemical composition that records the sum of many ongoing reactions.

Dramatic changes in the chemistry of interstitial water can occur as oxic sediments become suboxic or anoxic. The formation of an anoxic sedimentary environment is promoted by large inputs of organic matter. Because estuaries are especially prone to high loadings of nutrients and organic matter, decomposition reactions lead to oxygen depletion in sediments and sometimes in the water column. When oxygen depletion occurs in the water column it may result in hypoxia and fish kills. The Indian River Lagoon, on the east coast of Florida, is typical of many coastal estuaries where nutrient and organic matter loading are producing an environmental stress. This paper provides a preliminary view of chemical reactions in Indian River Lagoon sediments and how interstitial water studies can be applied to these systems.

Study Site — The Indian River Lagoon is a bar-built estuary that extends 200 km along the east coast of Florida. The lagoon has an average water depth of about 1 m with depths of 3 m or greater in the intracoastal waterway where dredging has taken place. Just three inlets connect the lagoon with the Atlantic Ocean. Thus, portions of the system are prone to water stagnation and are susceptible to the cumulative effects of nutrients and other species. Our sampling was carried out in the Eau Gallie River Basin (28° 07.4'N, 80° 37.6'W), located more than 30 km from the nearest inlet and further isolated by its location between two causeways across the lagoon. Previous work suggests that the area has been impacted by anthropogenic inputs (Trefry et al., 1983). Sampling for this study was designed to collect organic-rich sediment now found in many
areas of the lagoon. Water depths in the immediate study area are -0.6-2 m. The salinity of the
overlying water at this site ranges from 14-20°/ Tidal ranges in the Eau Gallie area are < 2 cm.

Methods — Sediment was sampled using a stainless steel box corer with dimensions of 50 x 50
x 40 cm. Two subsamples were carefully obtained from the box corer using 7.6-cm diameter
plastic tubes.

Interstitial water was obtained by using Teflon squeezers similar to those described by
Reeburgh (1967). Samples were processed in a nitrogen-filled glove box and filtered through 0.4
fim pore size Nuclepore filters. Squeezers, filters, and sample bottles were washed with dilute
HC1. Interstitial water was obtained from 0.5, 1, and 2-cm thick sections of the core, with the
sample interval increasing downcore. Water samples were stored at 4°C prior to analysis. Eh and
pH were measured at selected depths along a separate subsample by inserting the respective
probes into the sediment through pre-drilled holes in the plastic liner. These holes were taped
during sampling.

Concentrations of sulfide, ammonia, nitrate, nitrite, phosphate, silica, manganese, iron, sul-
fate and chloride were determined for each sample. Sulfide was measured using the methylene
blue method (Fonselius, 1976) combined with potentiometric standardization. Ammonia deter-
minations were made by the sodium hypobromite procedure (Guo and Gu, 1983) and dissolved
silica was measured with the silica-molybdate blue technique (Koroleff, 1976). Nitrite, nitrate
and phosphate were determined using standard colorimetric methods (Rand et al., 1975). Sulfate
concentrations were obtained with the turbidimetric method (Rand et al., 1975). Alkalinity was
determined with the pH technique (N.B.O., 1975) which was modified by standardizing the
dilute HC1 with a borax titration. After aliquots were drawn for the above measurements, the
remaining unaltered interstitial water was acidified with 100 /xl of concentrated, redistilled
HN0 3 . Manganese and iron determinations were made by atomic absorption spectrophotometry,
using flame and flameless techniques. The analytical precisions (coefficient of variation) for this
study are as follows: sulfide (5%), sulfate (2%), alkalinity (3%), dissolved silica (3%), ammonia (1%), phosphate (2%), chlorinity (1%) and manganese (1%).

Results and Discussion — The cores obtained from our study site in the Indian River Lagoon were composed of fine-grained, black, organic-rich sediment. During sampling, a strong H2S odor was detected throughout the core and no burrowing animal tubes were found within the sediment. The processed interstitial water had a slight yellow color suggesting high levels of dissolved organic matter.

In many estuaries, interstitial water chlorinity profiles record seasonal changes in the salinity of the overlying water. For example, in Chesapeake Bay, Matisoff and co-workers (1975) found an annual range of chlorinities in surficial sediment layers of 6-10.5 g/kg. At depths greater than 20 cm, the chlorinity was relatively constant near 10.5 g/kg, except at a shallow water station where chloride concentrations decreased downcore to as low as 2 g/kg. The observed seasonal differences in chloride values for surficial sediments (6-10.5 g/kg) could be related to variations in freshwater runoff to the bay and subsequent exchange between the interstitial and overlying waters.
The one decreasing chloride gradient observed was explained by seepage from a freshwater aquifer (Matisoff et al., 1975).

At our study site in the Indian River Lagoon, interstitial water chlorinity decreased linearly from 10.7-3.5 g/kg over the length of the core (Fig. 1). This decrease suggests that groundwater may be seeping through these sediments from below or that the water table is quite shallow at this location. Tidal pumping is not a significant variable at this location because the tidal range is < 2 cm. The chlorinity of lagoonal waters in this area is 8-11 g/kg (Trefry et al., 1983), values consistent with those for near-surface interstitial water. Conservative mixing of estuarine water and freshwater throughout the sediment column is a likely explanation for the observed chlorinity trend downcore. The chlorinity distribution at this site suggests that groundwater may play a role in controlling the salinity of these lagoonal waters.

Interstitial water pH was measured throughout the core and varied only slightly at 7.09 ±0.06. This value is consistent with calculations by Nissenbaum and co-workers (1972) which show that a pH of 7.0 should result when the products of marine organic matter decomposition equilibrate in seawater.

The redox potential (Eh) was also measured throughout the sediment column and values ranged from a high of -1 mV at 4 cm to -131 mV at 33.5 cm. A sharp drop in potential occurred over the 7-12 cm interval (Fig. 1). In natural water systems, the redox potential is often unstable and thus theoretical interpretation of Eh is difficult (Presley and Trefry, 1980). Nevertheless, a step-by-step chemical reduction sequence is often predicted from the range in potential over which a particular species can or cannot be oxidized (Stumm and Morgan, 1981). Several investigators have reported the disappearance of oxygen at Eh values below about + 250 mV, and that nitrate and manganese...
oxides begin to be chemically reduced (Eqn. 2 and 3) at slightly lower values (in Presley and Trefry, 1980). Iron oxides can be reduced (Eqn. 4) below +100 mV and sulfate reduction occurs at substantially lower values. Matisoff and co-workers (1975) observed a similar Eh profile in Chesapeake Bay to that shown for the Indian River Lagoon (Fig. 1) and found the onset of sulfate reduction occurred along a sharp Eh to -100 mV gradient.

Nitrate and nitrite concentrations were below detection limits (<0.2 μM) throughout the sediment column at our Indian River location. This depletion indicates that bacterial decay of organic matter was being carried out under suboxic or anoxic conditions and that the decomposition reaction had already shifted to Eqn. 3b or 4 in the surficial sediments. This condition results from high organic matter inputs to the sediments.

Under reducing conditions, nitrogen is regenerated as N₂ and NH₄⁺. At our study site, dissolved ammonia concentrations were found to increase from 1.1 mM at 0.5 cm to 5.3 mM at 39 cm (Fig. 1) with an average of 3.4 ±1.7 mM. Dissolved ammonia gradients were largest in the top 12 cm where sulfate reduction was most active (Fig. 1). Below 12 cm, complete sulfate reduction had occurred with a concurrent decrease in the ammonia gradient. Ammonia concentrations for our Indian River study site are comparable with
Fig 1. Vertical profiles showing interstitial water concentrations of chloride, silica, ammonia, alkalinity, sulfate, sulfide, theoretical sulfate, manganese, and Eh vs depth in the sediment column.
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those measured for the highly reducing sediments of Chesapeake Bay and Long Island Sound (Table 2).

The alkalinity of interstitial water increases as CO$_2$ is released from decaying organic matter. At our study site, alkalinity increased from 7.8 meq/liter in the top 0.5 cm to 23 meq/liter at 12-14 cm. The average pore water alkalinity for these sediments was 18 ± 5 meq/liter, about 8 times higher than normal seawater, yet comparable with other estuarine interstitial waters (Table 2). At pore water pH, the primary component of the alkalinity is HCO$_3$⁻.

In the top 6 samples (0-9 cm) the ammonia vs alkalinity relationship is a straight line ($r = 0.98$) with a slope of 6.1. Following the classic scheme for decomposition of organic matter (Richards and Cline, 1965), the ratio of inorganic carbon to ammonia is 6.6 (Eqn. 4), in reasonable agreement with the results of this study. No increase in alkalinity is observed below 13 cm; however, ammonia concentrations gradually increase downcore. This observation suggests that decomposition of organic matter is still proceeding, but the mechanism has changed. If so, methane generation via reduction of CO$_2$ (Table 1, Eqn. 6) is the most likely pathway. Methane generation is common in estuarine sediments after sulfate has been appreciably reduced (Kipphut and Martens, 1982). Although methane was not measured, the ammonia and alkalinity relationships and the absence of sulfate (Fig. 1) are consistent with the reduction of CO$_2$ to CH$_4$ as shown in Eqn. 6.

Accompanying each of the possible reaction pathways for organic matter decomposition is regeneration of inorganic phosphate from organic phos-
phorus. In the Indian River Lagoon, pore water phosphate concentrations ranged from 0.66-0.97 mM and averaged 0.76 ±0.12 mM. These values are 10-100 times higher than observed in estuarine waters, but are comparable with values from highly reducing estuarine sediments. Controls on interstitial phosphate concentrations are complex and may result from several reactions which control phosphate release to and removal from the interstitial water, including formation of an iron phosphate phase or adsorption of phosphate on sediment solid phases (Matisoff et al., 1980).

Dissolved silica concentrations in pore water can be enriched by the dissolution of biogenic silica as well as by release of dissolved silica from various silicate minerals. Silica concentrations are influenced by temperature, water composition, pH, sediment composition, and particle size (Fanning and Pilson, 1971; Matisoff et al., 1975). At our study site, dissolved silica values increase sharply in the top 2 cm and continue to increase gradually downcore to 1.4 mM at 39 cm (Fig. 1). The mean dissolved silica value for our core is very high at 1.1 ±0.2 mM. This value is much higher than commonly found in estuarine waters, somewhat higher than observed in estuarine interstitial water (Table 2), yet lower than the solubility of about 2 mM for amorphous silica.

Decreases in interstitial water sulfate concentrations are a good indicator of reducing conditions in estuarine sediments. The production of hydrogen sulfide during sulfate reduction is one of the more noxious and obvious results
of organic matter decomposition. At our study site, pore water sulfate concentrations decreased from 10.6 mM at the top of the core to essentially zero below 9 cm (Fig. 1). Throughout the core, including the top 1 cm, sulfate concentrations are much lower than those predicted from the \( \text{S}_2 \text{O}_4^2-/\text{C}_1 \) ratio for normal estuarine waters (0.140). At the top of the core, about one third of the sulfate has been reduced, as shown by comparing the theoretical sulfate profile (for the case where no sulfate reduction has occurred) with the observed sulfate distribution (Fig. 1).

Sulfate reduction leads to sulfide production.Interstitial sulfide concentrations at our study site increase from undetectable levels in the top centimeter to 1.7 mM at 13 cm. The sulfide produced is highly reactive and thus is not a reliable indicator of the extent of sulfate reduction. Sulfide can diffuse from the sediment column as \( \text{H}_2 \text{S} \) and contribute to the odor so commonly complained about along the Indian River; or it can precipitate in the sediments with metal ions, especially iron. Thus, we note that the moles of sulfate reduced are much higher than the moles of sulfide measured. Diffusion of sulfide downcore or possible influx of groundwater sulfide is evident in Fig. 1 since sulfide levels extend almost 30 cm deeper in the sediment column than the point of zero sulfate.

Metals such as Mn and Fe are usually present in the water column as oxides and hydrous oxides which exist as colloids or as surface coatings on
particles (Stumm and Morgan, 1981). Under reducing (suboxic or anoxic) conditions, these metals can be changed to a lower oxidation state and become more soluble. Manganese is especially susceptible to reduction and dissolution in environments such as the organic-rich, reducing sediments at our study site.

In our core, oxygen and nitrate were depleted in the top layers of the sediment and thus manganese oxide was used immediately as an oxidizing agent for organic decay. As a result, a maximum interstitial Mn concentration is reached in the top 0.5 cm with a steep decrease in Mn levels from 16-1 μM over a 6-7 cm interval. Below 9 cm, a relatively constant but 50 times lower concentration of 0.3 ±0.1 μM is observed. These values are all higher than normal seawater, but they are not especially high relative to other estuarine interstitial waters (Table 2). Such lower relative values for Mn in Indian River pore water most likely result from sediment Mn phases present and chemical reactions controlling interstitial Mn concentrations.

As concentrations of the various products of organic matter decomposition increase in the interstitial water, a series of second generation chemical reactions can occur. These reactions sometimes include formation of selected solid phases. Trace metals such as Mn or Fe, which are released to the pore water, may react to form solid phases such as oxides, carbonates, phosphates or sulfides.

The presence of several solid phases has been identified or implied for various estuarine and marine sediments. Bricker and Troup (1975) give evidence for the presence of an iron phosphate phase (vivianite) in Chesapeake...
Bay sediments. Similar studies, based on thermodynamic calculations, support the occurrence of a manganese phosphate phase in Lake Erie sediments (Matisoff et al., 1980). A manganese carbonate phase has also been postulated to form in anoxic marine sediments (Pedersen and Price, 1982). In anoxic sediments with high dissolved sulfide loading and higher Mn than Fe concentrations, Mn may precipitate as a manganese sulfide phase (Suess, 1979; Aller, 1980).

In our Indian River Lagoon pore water, Fe concentrations were <0.5 fM. Based on observed high sulfide levels of 0.01-1.7 mM and the solubility product for iron monosulfides, we predict an interstitial water Fe concentration of < 10^3 fM. This is certainly consistent with our measured Fe values.

To identify possible controls on interstitial water Mn values, a saturation index (SI) was calculated for three possible Mn phases:

\[ SI = \log(IAP/K_{sp}) \]  

where IAP is the calculated ion activity product for the species of interest and K_{sp} is the corresponding solubility product. A negative SI value indicates that the pore water is undersaturated with respect to a particular solid phase, whereas a positive value shows oversaturation. The three solid phases considered for Mn, along with their respective log K_{sp} values are as follows: MnC_0 \_3, -10.4 (Morgan, 1967); MnS, -17.8 (Aller, 1980); and Mn \_3 (P_0 \_4) \_2, -34.6 (Nriagu and Dell, 1974). All activity coefficients were corrected for changes in salin-
ity and pH and are as follows: phosphate, 2.46-30.6 x 10^-5 (Martens et al., 1978); carbonate, 0.053-0.74 (Pytkowicz, 1975); sulfide, 0.11-0.29 (Richards, 1965); and manganese, 0.29-0.40 (Morgan, 1967).

Calculated SI values for our study site (Fig. 2) suggest that the interstitial water is greatly undersaturated with respect to manganese carbonate and phosphate and that these solid phases would not be expected to form. In fact, the SI values for the carbonate and phosphate phases are always less than -1, suggesting that the Indian River Lagoon pore waters are at least 10 times undersaturated with respect to these phases. In contrast, our calculations support the formation of a Mn sulfide phase in the top 2-8 cm of the sediment column where SI values range from -0.2 to 0.5 (Fig. 2). Because the Indian River sediments were rich in sulfide and interstitial Fe concentrations were undetectable, the unusual prediction that manganese levels may be controlled by a sulfide phase is reasonable. It is certainly consistent with the work of Suess (1979) and Aller (1980).

The presence of high dissolved sulfide concentrations in lagoonal pore waters leads to precipitation of metal sulfides and the observed low interstitial water Fe concentrations of <0.5 fM. A similar trend of very low concentrations of elements such as Cd, Cu and Hg in the pore water is also predicted based on similar results by Elderfield et al. (1981) in Narragansett Bay. Thus the probability of metal release from such sediments is low and the sediments are an effective sink.

Previous studies of interstitial water chemistry in the Indian River Lagoon (Carlson et al., 1983; Montgomery et al., 1983) focused on sediments in fring-
Fig. 2. Plot of saturation for manganese phosphate (\(\square\)), manganese carbonate (I), and manganese sulfide (•) vs sediment depth. Saturation index (SI) = \(\log \left( \frac{\text{ion activity product}}{\text{solubility product}} \right) \).
Eau Gallie basin.

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ADDENDUM

Outstanding Student Paper Awards, Awardees

Fiftieth Annual Meeting of the Florida Academy of Sciences,

University of Florida, Gainesville — 10-12 April 1986

FCREPA — Blair E. Witherington, University of Central Florida, An Analysis of Reproductive Success in the Marine Turtle Nesting Aggregation at Melbourne Beach, Florida