

Biogeochemistry of organic-rich coastal lagoon sediments

Geochemistry
Organic matter
Sediments

Géochimie
Matière organique
Sédiments

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ABSTRACT

Geochemical processes in organic-rich lagoon sediments are dominated by the influence of microbially mediated degradation of recently deposited organic matter. A detailed study of chemical distributions and transport processes in a small coastal lagoon, Cape Lookout Bight, North Carolina (USA), reveals that degradation of the metabolizable fraction of the total organic matter not only controls interstitial water chemical composition, but drives the recycling of mobile degradation and products to overlying waters and the troposphere.

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RÉSUMÉ

Biogéochimie de sédiments lagunaires riches en matière organique

Les processus géochimiques dans les sédiments lagunaires riches en matière organique sont dominés par les phénomènes de dégradation d'origine bactérienne. Une étude détaillée de la composition chimique des sédiments et des phénomènes de transport dans une petite lagune côtière (Cape Lookout Bight, Caroline du Nord, États-Unis) montre que la dégradation de la fraction métabolisable de la matière organique contrôle non seulement la composition chimique de l'eau interstitielle mais également le recyclage des produits de dégradation dans la colonne d'eau sus-jacente et la troposphère.

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INTRODUCTION

Coastal lagoons act as natural traps for organic materials produced within their often fertile waters as well as for those entering from surrounding wetlands and terrestrial environments. Sedimentation of these organic-rich materials along with silts and clays is focussed on quiescent areas within the lagoon where power sources such as tides, waves and currents are minimized (e.g. Bokuniewicz, Gordon, 1980). The resulting organic-rich sediments are the site of intense microbially-mediated degradation processes which control sedimentary geochemical distributions and recycle vital nutrient elements and other mobile chemical end products to overlying waters.

In this paper we will focus on interpreting the chemical distributions found in the interstitial waters of organic-rich lagoon sediments in terms of the dominant microbially-mediated degradation processes. In addition, the mechanisms and rates of sediment-water recycling processes driven by these degradation reactions will be examined.

Relationships between organic matter degradation, interstitial water chemical distributions and sediment-water exchange processes are schematically illustrated in Figure 1 for the chemical system C-H-N-O-P-S-Fe-Mn. Numerous studies (e.g. Claypool, Kaplan, 1974; Martens, 1978; Froelich *et al.*, 1979) have demonstrated that the chemistry of organic-rich sediments is dominated by a sequence of respiration and fermentation reactions which begin with aerobic respiration (i.e. utilizing dissolved O_2 as oxidant) and utilize alternative electron acceptors such as dissolved NO_3^- and SO_4^{2-} under anaerobic conditions. When dissolved O_2 initially present in the interstitial waters of the sediments is exhausted, dissolved NO_3^- , solid phase Mn and Fe oxides, and dissolved sulfate are sequentially utilized before methane production occurs. This vertical sequence of oxidant utilization is indicated in Figure 1. The actual spatial and temporal distributions of the biogeochemical zones associated with the use of each oxidant (e.g. sulfate reduction zone) are controlled by the supply and subsequent degradation rates of metabolizable organic matter at any

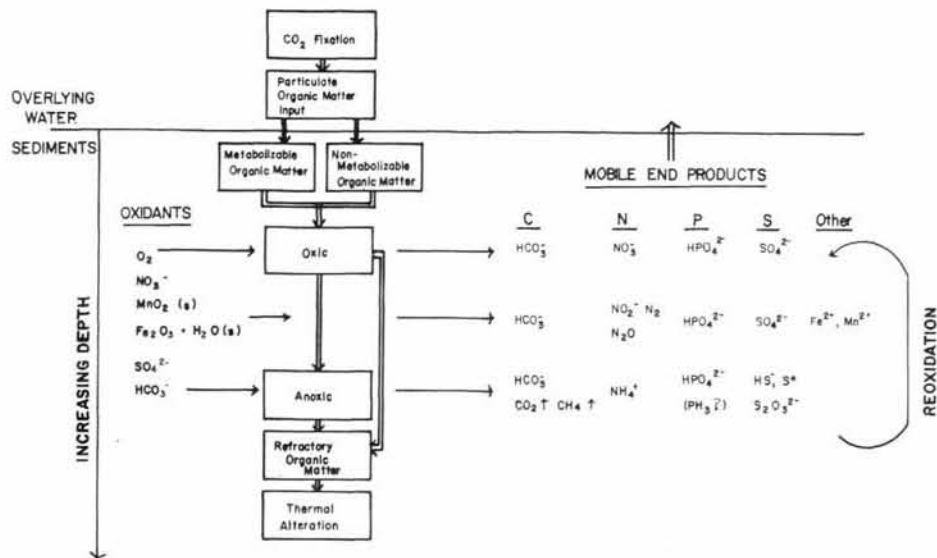


Figure 1 Schematic diagram of biogeochemical processes associated with the microbially-mediated degradation of metabolizable organic matter in organic-rich sediments.

single site. An increase in these rates drives the overall system towards more reducing conditions at shallower depths.

Major mobile chemical end products of the various respiration and fermentation reactions are included in Figure 1. These chemical end products such as dissolved inorganic carbon (ΣCO_2), NH_4^+ and reactive phosphorus (primarily HPO_4^{2-}) tend to increase in concentration with depth (and therefore time) in sediment interstitial waters. Their distribution in rapidly accumulating lagoon sediments can, in the absence of groundwater seepage, be expected to be controlled by a balance between their production rates and transport processes such as molecular diffusion and macrofaunal irrigation (Berner, 1971; Goldhaber *et al.*, 1977). Reduced chemicals diffusing or otherwise transported upward across the sediment-water interface to overlying waters are either oxidized near the sediment-water interface, taken up by benthic primary producers, or directly reenter the water column. The oxidation processes take place either inorganically or through microbial chem-lithotrophic processes in which primary producers derive their energy from the oxidation [e.g. Jannasch, Wirsén (1979)].

Quantitative descriptions of the mechanisms and rates of oxidation processes occurring at the sediment-water interface or in the water column remain as important research goals in lagoon systems as well as other organic-rich environments.

Recent work by our group at the University of North Carolina at Chapel Hill on Cape Lookout Bight, an organic-rich lagoon located on the Outer Banks barrier island chain along the east coast of the United States, can serve to illustrate some of the biogeochemical processes discussed above. The Cape Lookout Bight project has been designed primarily to quantitatively examine the coupling between production of mobile end products of organic matter degradation and transport processes recycling these end products to the water column. These processes take place in sediments whose accumulation rate and seasonal, chemical and macrofaunal characteristics are relatively well-defined.

THE STUDY SITE

Cape Lookout Bight is a small quiet water lagoon enclosed by an active, northerly migrating received spit. Its recent

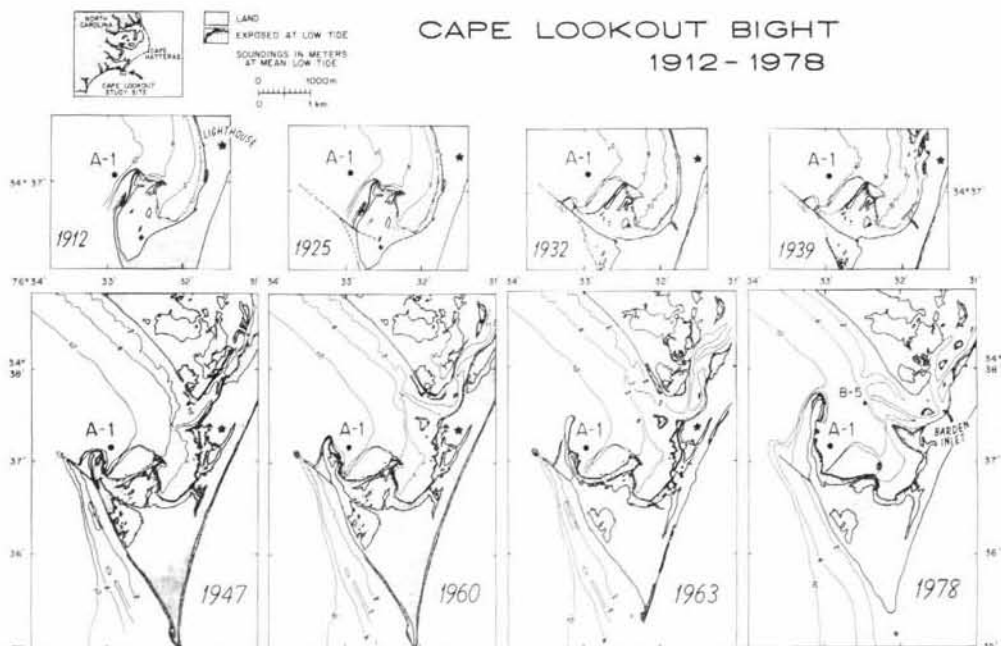


Figure 2 The recent geomorphological evolution of Cape Lookout Bight as seen through navigation charts since 1911 (Chanton *et al.*, 1982).

geomorphological evolution (Fig. 2) has been reviewed by Chanton *et al.* (1982). The bight traps organic-rich materials associated with silts and clays exiting to the Atlantic Ocean via Barden Inlet. The work discussed in this paper was conducted primarily at station A-1 located in the bight's interior (see Fig. 2). Current meter studies, sediment grain size distributions and benthic faunal populations were studied in a transect between stations A-1 and B-5. In the absence of storm activity, tidally controlled current speeds along this transect were dominated by a N-S component with a velocity of approximately 28 cm sec^{-1} at station B-5 which dwindles to velocities of less than 6 cm sec^{-1} at station A-1 (Martens, Klump, 1980). Benthic macrofauna along this transect are represented by more than 70 species in the sandy sediments of station B-5 while the silt-clay sediments of station A-1 contain only small ($< 2 \text{ cm}$ length) Spionid and Capitellid polychaete worms during winter-spring months (Bartlett, 1981). Station A-1 is devoid of benthic macrofauna throughout the summer and early fall months. It appears likely that a combination of highly sulfidic sediment chemical conditions and fish predation from well-oxygenated overlying waters produces the sudden disappearance of the dominant population of *Streblospio benedicti* polychaetes during late spring.

Organic matter decomposition processes at station A-1 occur primarily in association with sulfate reduction (Fig. 3). The sulfate reduction zone is observed to range from 0-10 cm depth during summer months to approximately 30-40 cm during winter months. Methanogenesis, which takes place primarily in sulfate-depleted sediments (Martens, Berner, 1974), occurs within 10-40 cm of the sediment-water interface during summer months with a maximum rate at 15-20 cm. During winter months methane production rates decrease and are restricted in large part to a narrow zone beneath the sulfate reducing sediments (Martens, Klump, 1980; Sansone, Martens, 1981; Crill, 1981, and unpublished data).

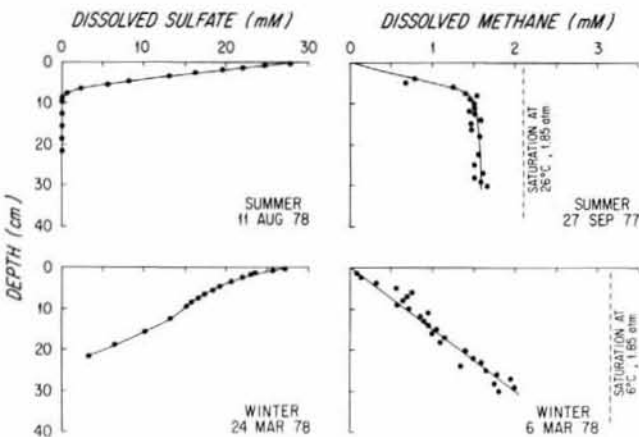


Figure 3
Seasonal variations in the depth distributions of dissolved sulfate and methane observed in the interstitial waters of station A-1 sediments.

A depth profile of the excess ^{210}Pb distribution (Fig. 4) in the silt plus clay fraction at station A-1 (Chanton *et al.*, 1982) serves to illustrate the relatively rapid and constant (i.e. nearly steady-state) sediment accumulation rate found there for the past decade. The mean value for total dry weight sediment accumulation since the late 1960's is $3.9 \pm 0.7 \text{ g cm}^{-2} \text{ yr}^{-1}$ which is equivalent to $9.8 \pm 1.7 \text{ cm yr}^{-1}$ of wet sediment with a mean porosity (volume water/volume total wet sediment) of 0.84. The upper 3 m are bifurcated by a series of sand layers thought to result from barrier island overwash processes occurring during severe storms (Chanton *et al.*, 1982). The shallowest of these layers, presently located at about 1 meter depth, is indicated by the excess ^{210}Pb data to be the result of the

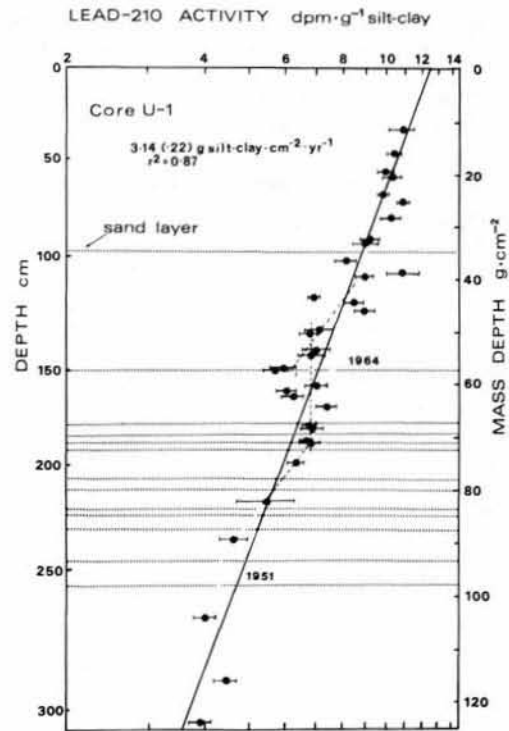


Figure 4
Excess lead-210 distribution in the silt-clay fraction plotted versus depth for station A-1 (Chanton *et al.*, 1982). The upper meter of sediment is approximately 95% silt plus clay and is accumulating at a rate of $9.8 \pm 1.7 \text{ cm yr}^{-1}$.

September 30, 1971 passage of Hurricane Ginger (Chanton *et al.*, 1982). The storm sand layers are easily detected by divers utilizing thin metal probes.

CARBON RECYCLING IN CAPE LOOKOUT BIGHT SEDIMENTS

Organic carbon content of the upper meter of station A-1 sediments (Fig. 5) is high, ranging from approximately 3.7% in the upper 0-0.5 cm to less than 2.5% at depths below one meter. These results indicate that approximately one third of the organic matter reaching the site is remineralized within ten years of deposition. Multiplying the ^{210}Pb total dry weight accumulation rate of $3.9 \text{ g cm}^{-2} \text{ yr}^{-1}$ times a mean organic C content of 2% at depth and changing units

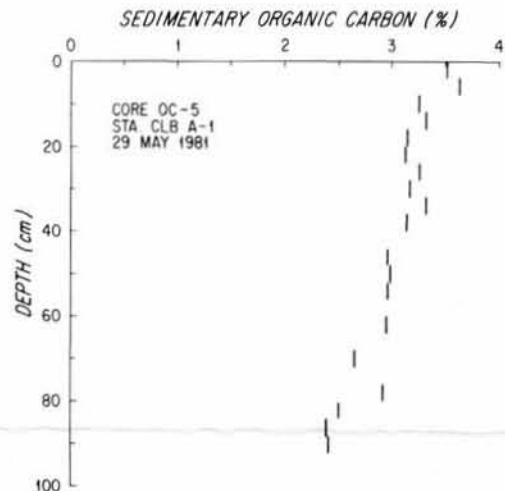


Figure 5
Sedimentary organic carbon content in the upper meter at station A-1 (Martens, Klump, 1981).

yields a carbon burial rate of $72 \text{ mole C m}^{-2} \text{ yr}^{-1}$ (Martens, Klump, 1981). We will compare this burial rate with measured fluxes of the remineralized organic carbon as ΣCO_2 (primarily dissolved HCO_3^- at pH 7-7.5) and CH_4 leaving the sediments to overlying waters.

Carbon fluxes across the sediment-water interface

Diffusive and gaseous bubble fluxes of ΣCO_2 and CH_4 at station A-1 during 1976-1980 were measured by diver-deployed benthic chambers and gas collection chambers suspended over the sediments as described by Martens and Klump (1980; 1981). The results are summarized in Figure 6. Seasonal variations in these observed fluxes are controlled primarily by temperature induced variations in rates of microbial ΣCO_2 and CH_4 production in the sediments. During summer months maximum rates and fluxes occur in association with high sediment temperatures peaking near 27°C ; during winter months, when temperatures occasionally drop below 5°C , minimum rates and sediment-water fluxes are observed. The seasonal variation in sedimentary organic matter degradation rates, R , can be modelled utilizing the Arrhenius rate law (e.g. Metzler, 1977):

$$\ln R/R_0 = -\frac{E_a}{RT} \quad (1)$$

where R_0 is the rate at some initial reference temperature ($\text{mole cm}^{-3} \text{ sec}^{-1}$), E_a is the Arrhenius activation energy (kcal mole^{-1}), R is the gas constant and T is temperature ($^\circ \text{K}$). A more correct treatment utilizes ΔH since $\Delta H = E_a - RT$; however at 25°C , RT is only 2.5 kJ mole^{-1} so ΔH is approximately equal to E_a . Typical E_a values observed for sedimentary processes such as sulfate reduction range from 18 to $25 \text{ kcal mole}^{-1}$ (e.g. Aller, Yingst, 1980).

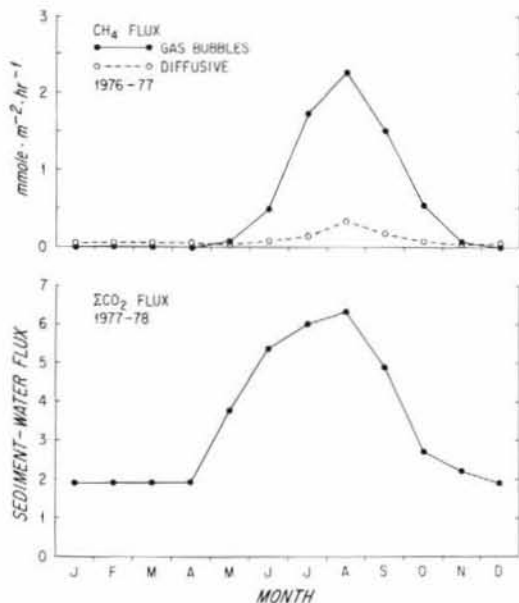


Figure 6
Sediment-water fluxes of ΣCO_2 and CH_4 at station A-1 (Martens, Klump, 1980; 1981). Diffusive ΣCO_2 fluxes dominate while the bubble CH_4 flux is approximately five times larger than the diffusive CH_4 flux.

Seasonal averages of ΣCO_2 and CH_4 fluxes at station A-1 yield the annual calculated fluxes listed in Table 1 (Martens, Klump, 1981). In order to calculate the fraction of carbon recycled in the upper meter of sediments we can compare the total carbon fluxes out as ΣCO_2 and CH_4 (J_{out}) with the incoming flux of solid phase organic carbon (J_{in}) arriving at the sediment water interface. During 1976 to 1980 the sum

Table 1

Annual average fluxes of dissolved and gaseous inorganic carbon and methane from station A-1 sediments to overlying waters.

	Mole $\text{m}^{-2} \text{ yr}^{-1}$
Dissolved ΣCO_2^1	29.8
Gaseous CO_2^1	0.06
Dissolved CH_4^2	0.85
Gaseous CH_4^2	4.85
Total	35.6

¹ Data from Martens and Klump (1980); ² Data from Martens and Klump (1981).

of J_{out} plus the carbon being buried (J_{bur}) as calculated above should equal J_{in} by simple mass balance:

$$J_{\text{in}} = J_{\text{out}} + J_{\text{bur}} \quad (2)$$

Therefore the fraction of carbon recycled which can simply be calculated as:

$$\% \text{ C recycled} = [J_{\text{out}}/J_{\text{in}}] 10^2, \quad (3)$$

becomes:

$$\% \text{ C recycled} = [J_{\text{out}}/J_{\text{out}} + J_{\text{bur}}] 10^2, \quad (4)$$

substituting J_{bur} and J_{out} values of 35.6 and $72 \text{ mole C m}^{-2} \text{ yr}^{-1}$ respectively into equation 4 yields a recycled organic carbon value of 33%. This result agrees with the one third decrease in % sedimentary organic carbon observed in the upper meter at station A-1 (Fig. 5).

Most importantly, the carbon budget tells us that only one third of the total organic carbon being deposited at our site achieves the fate expected for metabolizable organic materials (Fig. 1) which is to drive processes such as sulfate reduction and methanogenesis. The rest appears to be present as part of a non-metabolizable organic fraction destined to become buried until later diagenetic processes associated with much longer time periods and/or thermal alteration cause its breakdown. Models developed to quantitatively describe early diagenetic processes such as sulfate reduction (Bernier, 1974; 1980) are based on the fraction of metabolizable fraction present rather than the total which is generally measured. The observed change in organic carbon content with depth (Fig. 5) appears to be the simplest way to obtain estimates of the metabolizable fraction; however, this requires assumptions of a constant rate of supply of organic matter with an invariant blend of metabolizable and

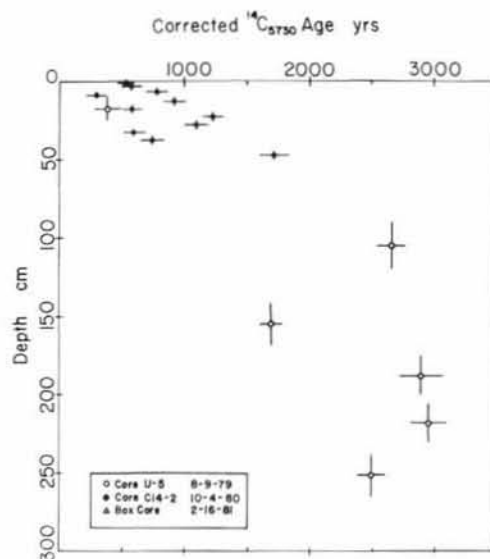


Figure 7
Radiocarbon age of organic carbon in the upper three meters at station A-1 (Martens, 1981). Ages Before Present (BP, 1950) were calculated using the true 5730 yr half life of ^{14}C and corrected for fractionation by $\delta^{13}\text{C}$ measurements.

Table 2.
Radiocarbon ages of some organic materials contributing to the total sedimentary organic carbon pool at station A-1.

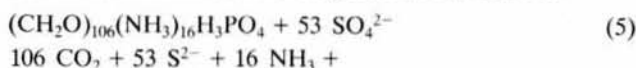
Organic material	Radiocarbon age (years B.P. 1950)
Mixed salt marsh grasses ¹	-2.207 ± 66
Wet seagrass debris ¹	-1.120 ± 58
Living <i>Zostera marina</i> ¹	-1.290 ± 74
Shoreline peats ²	200 - 5,000
Soil carbon ³	0 - 5,000
Zooplankton ³	-1.030 ± 80

¹ Data from Martens (1981); ² See Martens (1981) for data and references to previous work; ³ Data from Benoit et al. (1979) and references therein, the zooplankton result is from Long Island Sound.

non-metabolizable components. These assumptions are difficult to accept for lagoon sediments influenced by a variety of terrestrial, anthropogenic and marine input processes. Radiocarbon dating of sedimentary organic carbon provides a potentially important method for more direct determination of the source or sources of organic carbon undergoing degradation and conversion to ΣCO_2 and CH_4 in the sediments. Preliminary radiocarbon ages for sedimentary organic carbon in the upper three meters of station A-1 sediments (Fig. 7) illustrate the power of this tool. The Cape Lookout environment receives organic carbon materials with ages similar to those listed in Table 2. Recently produced plankton, seagrass and salt marsh plants are highly enriched in ^{14}C put into the atmosphere by nuclear weapons testing. In fact these "bomb carbon" enriched materials have negative ages because their ^{14}C content is above that expected for plant tissues in equilibrium with the prebomb atmospheric ^{14}C concentration (Faure, 1977). The plankton, seagrass and marsh plant components appear to be preferentially degraded in the upper meter of sediments while older soil and/or shoreline peat derived materials with radiocarbon ages of about 3,000 yrs are preserved at depth. The conclusion drawn from these results is that the major fraction of the metabolizable organic material, composed of recently produced bomb ^{14}C enriched seagrasses, plankton and salt marsh plant debris, is recycled on a time scale of less than ten years (1 m depth @ 10 cm yr⁻¹ sediment accumulation rate).

NUTRIENT RECYCLING FROM ORGANIC-RICH LAGOON SEDIMENTS

During aerobic respiration, sulfate reduction and the other respiration and fermentation processes summarized in Figure 1, the nutrient elements N and P included as part of proteins, carbohydrates and other molecular structures are released. The overall stoichiometry of these reactions can be represented by equations in which idealized organic matter with a Redfield C:N:P ratio composition (Redfield *et al.*, 1963) is degraded utilizing the oxidants listed in Figure 1. For example the reaction utilizing dissolved sulfate as oxidant could be represented as follows:



Under anoxic sulfate reducing or methanogenic conditions such as those found within the Bight's sediment column, the dominant dissolved N and P compounds formed are NH_4^+ and HPO_4^{2-} as indicated in equation 5. Temperature dependent seasonal production rates of these degradation end products as discussed above, coupled with sediment-water exchange processes lead to pronounced seasonal variations in their vertical concentration distribution. This

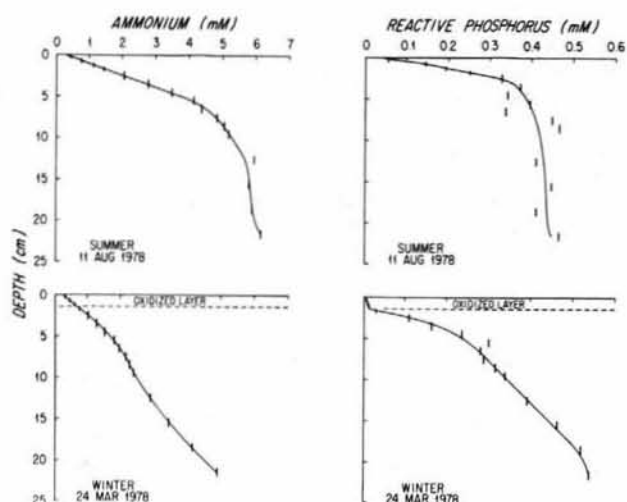


Figure 8
Dissolved NH_4^+ and reactive phosphorus (primarily HPO_4^{2-}) distributions in the upper 30 cm of interstitial waters at station A-1 (Klump, Martens, 1981). Concentration gradients were fit utilizing equation 6 except for winter phosphorus data which were linearly fit in the upper few cm.

can be seen at our Cape Lookout study site as illustrated in Figure 8. These concentration profiles can be used in combination with Fick's first law of diffusion, modified for sediments as discussed by Berner (1971; 1980), to predict minimum fluxes to overlying waters:

$$J = -\phi D_s \left(\frac{\partial C}{\partial z}\right)_{z=0}, \quad (6)$$

where J is the upward nutrient flux ($\mu\text{mole m}^{-2} \text{h}^{-1}$), ϕ is porosity, D_s is the whole sediment diffusion coefficient corrected for sediment grain effects ($\text{cm}^2 \text{sec}^{-1}$) and $(\partial C/\partial z)_{z=0}$ is the nutrient concentration gradient immediately at the sediment-water interface. This latter gradient can be determined by curve fitting the concentration data in Figure 8 with an equation of the form:

$$C_z = (C_0 - C_\infty) \exp -\alpha z + C_\infty, \quad (7)$$

where C_z , C_0 and C_∞ are nutrient concentrations at depth z , the sediment-water interface (usually assumed to be the

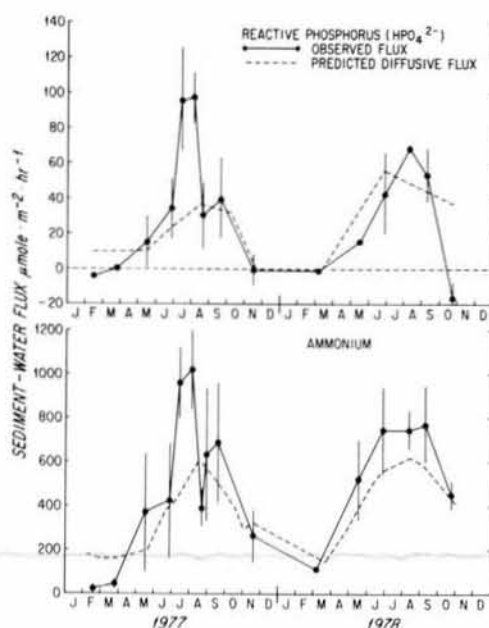


Figure 9
Dissolved NH_4^+ and reactive phosphorus fluxes observed at station A-1 utilizing benthic chambers and predicted by equation 6 (Klump, Martens, 1981).

overlying water value) and at some depth where the concentration gradient approaches zero. Both the attenuation constant α (cm^{-1}) and C_z are obtained by an error minimization computer routine which also yields calculated values for $(\partial C/\partial z)_z = 0$.

Fluxes measured by benthic chambers (Klump, Martens, 1981) and theoretical fluxes calculated from equation 6 for NH_4^+ and HPO_4^{2-} are shown in Figure 9. Fluxes above equation 6 predictions during summer months for both NH_4^+ and HPO_4^{2-} appear to result from non-uniform physical structure and chemical distributions in the upper 10 cm of sediments. In particular, methane bubbles exiting the sediments during low tides create open bubble tubes, 2-20 mm in diameter and up to 10 cm deep which act as conduits for enhanced vertical chemical exchange (Martens, Klump, 1980; Klump, Martens, 1981).

During winter months, observed HPO_4^{2-} fluxes below those predicted by molecular diffusion (equation 6) apparently result from scavenging of HPO_4^{2-} from solution by iron oxyhydroxides precipitating in the upper few cm of sediments where downward penetrating dissolved O_2 is reacting with upward diffusing ferrous iron.

Approximately 39 and 15% of the N and P deposited at station A-1 are recycled to the water column according to the calculations of Klump (1980). These recycled nutrients can supply more than 50% of the nitrogen demand of primary producers in nearby overlying lagoon waters (Smith, 1975).

TRACE GAS FLUXES FROM LAGOON SEDIMENTS TO THE TROPOSPHERE

The methane-rich gas bubble transport from Cape Lookout Bight sediments represents a potentially important mechanism for dissolved gas exchange between lagoon sediments and the troposphere. Such processes, which may be of widespread importance in organic rich lagoon environments, have only recently begun to be studied in any detail. Methane bubbles produced in the sediments strip other dissolved gases in surrounding interstitial waters from solution. The upward migrating bubbles subsequently transport these stripped gases, including N_2 , Ar and CO_2 , out of the sediments. The radioactive noble gas, radon-222, has been utilized by our group to quantitatively examine this process (Kipphut, Martens, 1982). Dissolved radon-222 is present in sediment interstitial waters at concentrations orders of magnitude above overlying water concentrations because of the concentration of its parent isotope, radium-226, in the sediments on fine gradined sediment particle surfaces. The actual distribution of radon-222 in sediments is controlled by a balance between production from radium-226, its own radioactive decay (Rn-222 half life = 3.825 days) and transport processes. Below approximately 6-10 cm, the radon-222 activity should be approximately

equal to radium-226 activity in the absence of other transport processes (i. e. secular equilibrium is attained). Correlations between methane bubble production and radon-222 deficiencies in the sediments beneath 8 cm at our study site (Fig. 10) reveal the influence of the microbial processes on trace gas transport processes. A deficit corresponding to the loss of a few percent per day of the radon-222 results from bubble stripping; deficits resulting from molecular diffusion near the sediment-water interface and in the methane bubble production zone are depicted in Figure 11. The bubble stripping process accounts in the same manner for the removal of approximately 2% per day of the dissolved N_2 in the depth range of 10-30 cm. Any dissolved gases diffusing into methane saturated lagoon sediments as in the case of N_2 or produced within the sediments themselves as in the case of radon-222, H_2S and others have a significant probability of being transported directly to overlying waters and the troposphere.

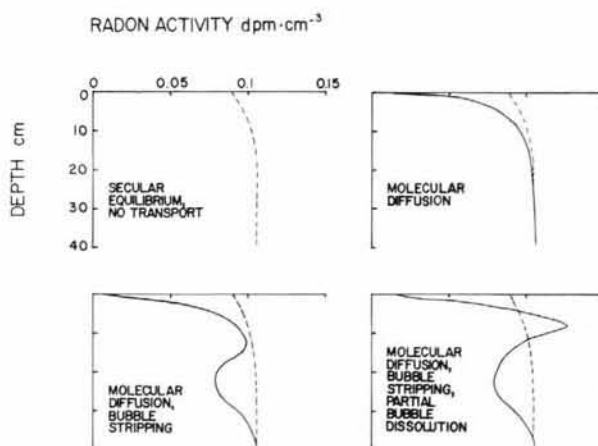


Figure 11

Schematic diagrams illustrating the processes controlling the distribution of dissolved radon-222 in the interstitial waters of station A-1 sediments: a) production from radium-226 with no transport; b) production plus molecular diffusion across the sediment-water interface; c) production, molecular diffusion, bubble stripping and rising bubble dissolution in methane-undersaturated sediments above the zone of methane production.

SUMMARY AND CONCLUSIONS

The microbially-mediated degradation of metabolizable organic materials in organic-rich lagoon sediments exerts important influences on the chemical composition of sediments, lagoon waters and the troposphere. These chemical influences include controls on the relative importance of aerobic versus anaerobic respiration/fermentation processes within the sediments, and the recycling of mobile degradation end products to sediment interstitial waters, overlying waters and the troposphere. All of these processes are driven by the rate of supply of metabolizable organic matter, whose distribution is, in turn, controlled by physical and geological processes.

Our ability to predict changes in the geochemistry of lagoon sediments brought about by the addition of metabolizable organic matter is directly tied to our ability to quantitatively model the dynamics of degradation processes and their chemical end products as well as a variety of transport phenomena. In comparing sedimentary systems with similar transport regimes we can generalize using Figure 1. Increasing additions of metabolizable organic matter should drive the system down the list of oxidants and mobile chemical end products towards more reducing conditions. This latter effect is an important factor in determining the distributions and species composition of both microbial and macrofaunal benthic populations.

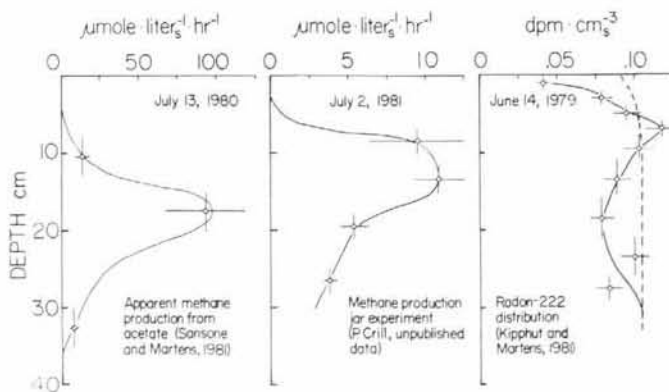


Figure 10

Methane production rates from: a) Sansone and Martens (1981); b) Crill (1981, and unpublished data); compared with summertime radon-222 deficit; c) observed by Kipphut and Martens (1982).

Acknowledgements

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