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Comparative biogeochemistry of water in intertidal *Onuphis* (polychaeta) and *Upogebia* (crustacea) burrows: temporal patterns and causes

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ABSTRACT

The burrows of macrobenthos represent an important class of sedimentary microenvironments which significantly influence chemical, biological, and physical characteristics of a deposit. In intertidal regions, the time-dependent changes in composition during ebb-tide of water contained in burrows is a sensitive indicator of biogenic and abiogenic chemical reactions in burrow walls and adjacent sediment. Comparison of time series water samples taken from *Onuphis jenneri* (polychaete) and *Upogebia affinis* (crustacean) burrows in the same tidal flat demonstrate substantial differences in biogeochemical microenvironments despite the spatial proximity of the two species. Both types of burrows are influenced by the same general kinds of biogeochemical reactions but the relative intensity of these reactions differs in each case. Evidence for both heterotrophic and chemoautotrophic metabolic activity in each burrow type comes from the build-up or consumption patterns in burrow water of solutes such as NH_4^+ , NO_3^- , Mn^{++} , I^- , HPO_4^- , and HCO_3^- . Burrow irrigation models and the stoichiometry of solute build-up imply that *Upogebia* burrows are sites of more intense nitrification-denitrification and microbial activity generally than are *Onuphis* tubes. *Upogebia* burrow water is also distinctly undersaturated with respect to carbonate minerals and has high numbers of bacteria relative to *Onuphis*. In addition to reaction rates, burrow geometry and the adsorption-diffusive permeability properties of the burrow wall also affect transient behavior of solutes. The organic burrow lining of *Onuphis* shows linear adsorption isotherms for positive, negative, and neutrally charged solutes represented by NH_4^+ , HPO_4^- , and $\text{Si}(\text{OH})_4$. Diffusion-reaction modeling demonstrates that adsorption, in particular, can significantly lower the transient state concentrations of burrow water trace solutes even for tube wall thicknesses of only 200 μm . The observed differences between burrow microenvironments of the two species living in close proximity suggest distinct biogeochemical associations between microbes and species specific biogenic structures.

1. Introduction

Most surficial marine sediments can be viewed as a mosaic of physical and chemical microenvironments created in part by the organisms which live there. The bulk physical-chemical properties of a deposit, certain kinds of ecological interactions

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between inhabitants, and physiological adaptations of individual species are determined by the characteristics of these microenvironments (Jumars, 1975; Jørgensen, 1977; Anderson and Meadows, 1978; Aller and Yingst, 1978; Aller, 1982; Reise, 1981a). Burrows and tubes of infaunal, macroinvertebrates represent one important class of such small scale biogenic structures. A typical burrow or tube structure is composed of a central, irrigated shaft in which the inhabitant lives and a portion of the immediately surrounding sediment with which it interacts. In the present study we emphasize properties of the central axes of representative burrow microenvironments, first documenting variations in the chemical composition of water contained in burrows of two species from a single intertidal habitat and then examining the controlling factors and implications. Our basic approach is to utilize the natural tidal cycle, which connects and disconnects burrows from the overlying water reservoir, to obtain an incubation time series of burrow water samples. The time dependence of burrow water solute concentration is determined in part by solute fluxes between the irrigated burrow core and surrounding sediment and thus is a measure of reactions in the burrow wall. The role of adsorption-desorption properties of tube linings in modifying transient variation of burrow water composition is also considered.

The species chosen for study are *Onuphis jenneri*, an onuphid polychaete worm, and *Upogebia affinis*, a thalassinid shrimp. Both are either common inhabitants or closely related to other common inhabitants of intertidal sands and muds in relatively high salinity portions of estuaries along the southeast coast of North America (Pearse, 1945; Smith, 1967; Hertweck, 1972; Howard and Frey, 1975; Gardiner, 1975). *Onuphis* forms a vertically oriented tube composed of an inner polysaccharide lining ~20 μm thick and an outer agglutinated sandy layer, usually one to two grains across, of ~200 μm thickness. Tubes typically have inner diameters of 0.3–0.4 cm and taper upward for the last 2–3 cm where they may or may not project above the sediment-water interface for several centimeters. They can extend ~70 cm into a deposit and individual animals can be several decimeters long. The related form *Onuphis microcephalata* has been described as a suspension-feeder (Pryor, 1975) or carnivore (Howard and Frey, 1975) and other onuphids are of varied trophic type (Fauchald and Jumars, 1979). The common occurrence around onuphid tubes of well-sorted, fecal piles composed exclusively of fine material comparatively rare in the surrounding deposit, the tapered-tube opening which enhances terminal irrigation velocity, and the tendency for animals to be relatively sedentary imply that in this case *Onuphis jenneri* is a suspension feeder.

Upogebia affinis, sometimes called the mud shrimp or mud lobster, forms a complex burrow system having multiple openings and chambers; Y-shaped portions and branches may extend several decimeters laterally and vertically (Pearse, 1945; Smith, 1967; Frey and Howard, 1975). Some sections of the burrow wall are reinforced, or cemented, several centimeters outward into the surrounding sediment. The inner burrow wall is not lined with a distinct membrane but is quite smooth in texture and

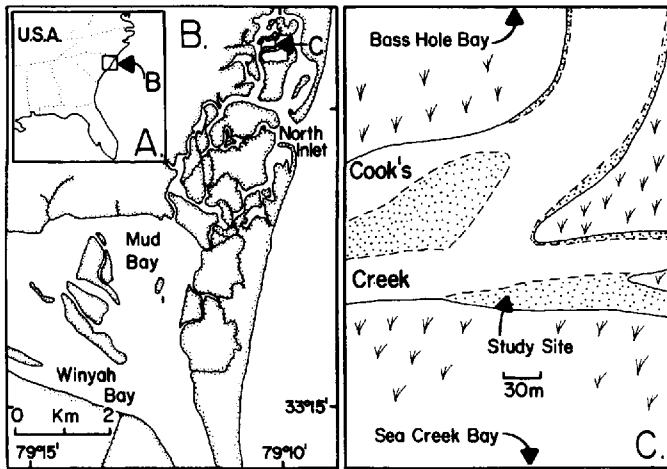


Figure 1. (A) Location of South Carolina on southeast coast of U.S.A. (B) Coast of South Carolina showing location of Winyah Bay–North Inlet estuaries. North Inlet area indicating location of Cooks Creek [inset C]. (C) Sketch of Cooks Creek intertidal study area.

may be enriched with organic matter relative to surrounding sediment (Thompson, 1972). Burrow openings at the sediment-water interface are typically 0.5–1 cm diameter in the study area, but burrow shafts often expand to 1–2 cm diameter a few centimeters below the surface. The adult animal itself is usually ≥ 5 cm in length in the study area. There appear to be ~ 6 –8 surface openings to a single burrow scattered in an overall elliptical area but this may change seasonally. More than one individual may be associated with a burrow complex (Jenner, 1977). *Upogebia* has been called a suspension feeder (MacGinitie and MacGinitie, 1968), but it has also been suggested that members of the genus garden bacteria from decomposing algae along burrow walls (Frey and Howard, 1975; Ott *et al.*, 1976).

2. Study area

The study area is located on a single tidal flat along Cooks Creek in the North Inlet back-barrier complex near Georgetown, South Carolina (Fig. 1). The exposed flat is roughly triangular in plan view and adjoins *Spartina* marshes on its southern and western edges. The topographic gradient is low (~ 1.5 cm/m) so that most of the flat is exposed or flooded within ~ 1 hour. Sediment grain size varies considerably over the flat, tending to be muddier in the more eastern portion and along the low water and marsh borders. In the actual sampled area, average grain size is a relatively uniform fine sand with a mean size of ~ 0.145 mm. It is moderately to moderately well sorted and skewed to the silt size range which averages $\sim 9\%$ by weight. While Creek salinity is usually high (~ 31 – 34‰) with $\text{Cl}^- \sim 0.5$ – 0.54 M (M = moles/liter) and yearly

temperatures range between $\sim 10\text{--}30^\circ\text{C}$, there can be marked excursions in these water properties depending on weather patterns.

3. Sampling and methods

a. Burrow and overlying waters. A time series of burrow water composition during ebb tide was obtained by first placing time-labeled markers next to burrows just as they were exposed by the receding tide. Individual burrows were then sampled at various intervals after initial exposure to provide a complete spectrum of possible incubation times. Care was taken to randomize sampling spatially in order not to bias any temporal patterns. Samples were obtained by inserting either a thin plastic tube (~ 1 mm diameter) directly into a burrow and withdrawing water into a plastic syringe or, in the case of some *Onuphis*, allowing the animal to pump water out of its tube following disturbance and removing water from the opening as it exited. Sampling tubes were inserted an average of $\sim 24 \pm 8$ cm into *Upogebia* burrows. Each time sample for *Onuphis* represents water combined from 2 to 10 individuals while those for *Upogebia* each come from a single burrow system. Generally ~ 5 ml/individual *Onuphis* were obtained but a range of $\sim 3\text{--}10$ ml occurred. A total of ~ 20 ml of burrow or tube water was collected for each time interval.

Overlying water samples were also collected at various times as the tide receded. These were taken a few centimeters above the bottom to closely correspond to water that actually entered burrows. Overlying water samples were subsequently treated in the same way as burrow waters.

Onuphis tubes were sampled during both summer 1979 (water $T \sim 24^\circ\text{C}$) and winter 1980 (water $T \sim 10.5^\circ\text{C}$) on July 8, 1979 (chemical analysis only), July 19, 1979 (bacteria only), and February 15, 1980. A total of 64, 30, and 78 individuals were sampled on these dates respectively. *Upogebia* burrow waters were sampled on July 11, 1979 for chemical analyses (10 burrows) and July 19, 1979 for bacteria (9 burrows). Not enough open *Upogebia* burrows could be found during winter 1980 to allow adequate time series sampling.

A small portion of each sample used for chemical analyses was immediately expressed into a specially designed plastic chamber and the pH measured using a semi-micro combination glass electrode (Corning, Ag-AgCl reference). The remainder was filtered through an in-line $0.4 \mu\text{m}$ pore size Nuclepore filter directly into a receiver syringe and stored on ice in the dark until returned to the lab for analysis. Water samples used for enumeration of bacteria were immediately placed on ice in the dark. Upon return to the lab, they were allowed to settle briefly until no suspended macroscopic particles could be seen; the supernatant was then injected into a receiver syringe containing gluteraldehyde to produce a final solution of $\sim 0.3\%$ with preservative. On 15 February 1980, several overlying water samples were centrifuged for 10

minutes upon return to the laboratory and then preserved for comparison with gravity settled samples.

Filtered water samples were analyzed for NH_4^+ , $\text{NO}_2^- + \text{NO}_3^-$, HPO_4^- , $\text{HCO}_3^- + \text{CO}_3$ (alkalinity), SO_4^- , $\text{Si}(\text{OH})_4$, Cl^- , $\text{I}^- + \text{IO}_3^-$, Fe^{++} , and Mn^{++} . The methods used were NH_4^+ -phenolphthorite (Solórzano, 1969; Degobbis, 1973), $\text{NO}_2^- + \text{NO}_3^-$ -ethylenediamine dihydrochloride (modified from Strickland and Parsons, 1968); HPO_4^- -molybdate (Strickland and Parsons, 1968), alkalinity-HCl titration (Gieskes and Rogers, 1973), SO_4^- -gravimetric BaSO_4 , $\text{Si}(\text{OH})_4$ -reduced molybdate (Strickland and Parsons, 1968; Fanning and Pilson, 1973), Cl^- - AgNO_3 /starch/fluorescein, I^- - Ce/As catalysis (Barkley and Thompson, 1960; Ullman and Aller, 1980), Fe^{++} -atomic adsorption, and Mn^{++} -atomic adsorption. In each case the published method was modified slightly to accommodate small sample size. Analytical precision is estimated at $\leq 1\%$ for alkalinity, $\text{Si}(\text{OH})_4$, and Cl^- , $\leq 3\%$ for NH_4^+ , I^- , and SO_4^- , and $\leq 10\%$ for HPO_4^- , $\text{NO}_2^- + \text{NO}_3^-$, Fe^{++} , and Mn^{++} based on other analyses at the concentrations and sample sizes used; duplicates could not be run in most cases.

Preserved bacteria samples were filtered and stained with acridine orange (Hobbie et al., 1977; Watson et al., 1977). Bacteria were then counted using epifluorescence microscopy. Counts of 500–1000 cells per sample were made by examining alternate fields along transects from the center to the margins of each filter. The number of cells per ml water was then calculated based on the volume filtered (2 to 5 ml for burrow water, 10 ml for overlying water). Duplicate precision is $\leq 5\%$, based on equivalent numbers of counts made on other samples.

b. Adsorption—desorption experiments. The adsorption behavior of *Onuphis* tube linings with respect to NH_4^+ , $\text{Si}(\text{OH})_4$, and HPO_4^- compared with surrounding sediment was examined in several experiments. Known total lengths, generally 7–8 cm, of *Onuphis* tubes were placed in a series of scintillation vials, each containing 4 ml of a standard solution. These tubes had been previously preserved in 0.2% glutaraldehyde sea water and kept in a refrigerator. They were rinsed in filtered sea water and shaken free of water before use. Mixed standard solutions were usually made up in filtered (0.4 μm), natural sea water from the North Inlet region ($\text{Cl}^- = 0.417 \text{ M}$; pH range of standards = 7.9–8.6) and known amounts of NH_4^+ , HPO_4^- , and $\text{Si}(\text{OH})_4$ added. One set of $\text{Si}(\text{OH})_4$ alone adsorption experiments was done in distilled water (pH = 5.7–5.9). The starting concentrations in the mixed standard series were: 14.7, 29.4, 44.0, 58.7, 117, and 176 μM for NH_4^+ ; 5.3, 10.5, 21.1, 31.6, 52.6, and 105 μM for HPO_4^- ; and 14.2, 28.5, 71.2, 142, 214, and 356 μM for $\text{Si}(\text{OH})_4$ respectively.

After adding the tube section to a vial, the sample was shaken then placed in an incubator at $T = 25^\circ\text{C}$ for periods of 2–2.5 hours depending on the experiment. In the distilled water experiment samples were equilibrated for periods of 1 hour to 4 days. Vials were agitated periodically during incubation. A series of control vials containing standards but no tubes was always incubated at the same time. At the end of the

incubation period, water in the vials was analyzed and the adsorption-desorption of NH_4^+ , HPO_4^- , and $\text{SI}(\text{OH})_4$ calculated by difference relative to control values.

The agglutinated sand layer was not completely separated from the inner lining in most cases. In order to evaluate the relative role of organic lining to sand particles in determining adsorption behavior of the lining, the outer layer was carefully scraped off for the most part in one experiment and in another only the sand fraction of sediment from the tidal flat was used. At the end of the various experiments the tube sections or sediment samples were rinsed, dried, weighed and analyzed for organic carbon by wet oxidation (Gaudette *et al.*, 1974). The inorganic, acid-insoluble residue (mostly quartz sand) remaining after the organic C analysis, was weighed and the relative abundance of sand and organic matter in each vial calculated. This allowed normalization of the adsorption-desorption properties to either tube length, total dry weight, weight of organic carbon, or sand fraction.

4. Results

a. Burrow water composition. Solute concentrations in burrow waters are plotted as a function of incubation time during ebb tide in Figures 2–12. Tabulations of SO_4^- and Cl^- concentrations are given in Table 1 and are essentially constant. Comparatively small individual volumes of winter burrow water samples did not allow the full range of analyses done for summer samples.

The solute compositions of *Onuphis* and *Upogebia* burrow waters have similar concentration ranges and temporal patterns of change in some cases but differ substantially in others. *Upogebia* burrows generally show greater scatter in time-dependent patterns presumably due in part to complex variation in burrow geometry. The water in both burrow types is significantly more acid than overlying water with pH values at least 0.5 units lower at time of first exposure. The pH of *Upogebia* burrow water continues to drop significantly after irrigation ceases and reaches values as low as 7.2 in 140 minutes (Fig. 2). In contrast, *Onuphis* burrows show either a constant pH of ~7.6 or a modest rise over 220 minutes. This upward shift is within the range of overlying water variability and may or may not be a real increase. The shift may also be due to electrode drift rather than real variability in either overlying or burrow waters. Field conditions did not allow measurement of burrow water pH on the flat during winter 1980 (15 Feb.). Measurements made in the laboratory indicated that *Onuphis* waters ranged from 7.69–8.00 compared with an overlying water range of 7.98–8.11. These imply that burrow pH values are both higher and differ less from overlying water during winter than summer, but possible CO_2 degassing during storage prevents much confidence in this observation.

Titration alkalinity ($\sim\text{HCO}_3^- + 2\text{CO}_3^-$) demonstrates that *Onuphis* burrows differ little from overlying water during summer but may have substantial relative elevations in this property during winter (Fig. 3A). Normalization of alkalinity to Cl^-

Table 1. Overlying tidal flat water, Cooks Creek and burrow water samples of *Onuphis jenerri* and *Upogebia affinis* during July 1979 and February 1980.

<i>Onuphis jenerri</i>				<i>Upogebia affinis</i>								
July 1979			February 1980			July 1979						
t (minutes exposed)	Cl ⁻ (M)	SO ₄ ⁻ (mM)	CO ₂ * (μM)	t (minutes exposed)	Cl ⁻ (M)	t (minutes exposed)	Cl ⁻ (M)	SO ₄ ⁻ (mM)	CO ₂ * (μM)			
10	0.518	26.8	63.5	5	0.513	10	0.499	24.0	77.2			
40	0.535	27.9	59.8	15	0.509	20	0.516	26.0	76.2			
50	0.529	27.0	59.9	30	0.513	55	0.509	27.0	137			
80	0.533	26.8	61.7	50	0.506	70	0.524	26.1	132			
100	0.535	27.0	54.3	59	0.513	85	0.509	26.3	105			
130	0.533	27.4	49.8	72	0.499	95	0.521	27.0	108			
135	0.535	27.4	48.3	93	0.506	105	0.523	25.9	112			
135	0.529	27.2	54.7	112	---	120	0.518	26.1	117			
150	0.530	26.4	52.7	124	0.506	135	0.506	25.9	111			
160	0.534	25.7	47.9	139	0.499	140	0.523	26.8	168			
171	0.529	27.4	53.5	162	0.520							
190	0.525	26.4	49.3	183	0.482							
205	0.528	27.0	51.9	198	0.511							
220	0.532	27.2	49.2	212	0.495							
				225	0.506							

Overlying Water			Sample			Sample					
Sample			Sample			Sample					
1	0.538	28.0	1	0.510		1	0.531	---	29.9		
2	0.539	27.9	2	0.513		2	0.534	---	34.7		
3	0.539	28.3	3	---		3	0.531	---	34.7		
4	0.539	28.0	4	---							
5	0.538	28.1									

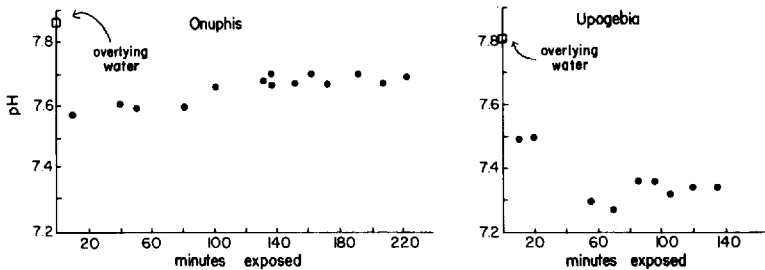
*CO₂ = CO₂ + H₂CO₃

Figure 2. Overlying and burrow water pH as function of time of exposure (summer 1979).

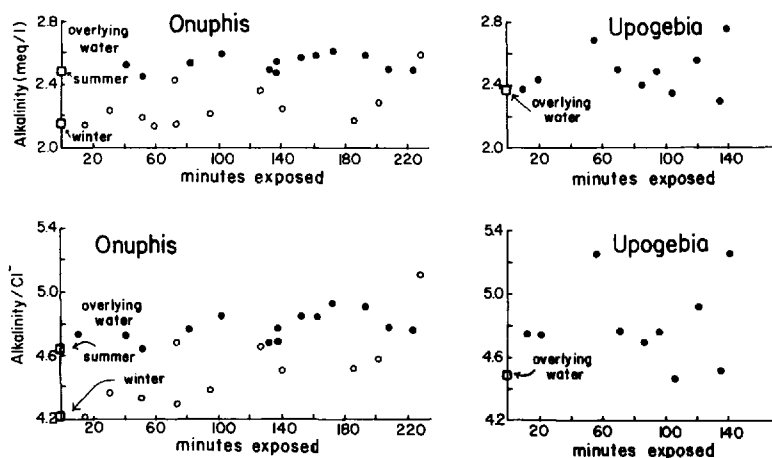


Figure 3. Titration alkalinity and alkalinity/ Cl^- ratios in *Onuphis* and *Upogebia* burrows. Solid circles = summer 1979; open circles = winter 1980; open squares = overlying water. (meq/l = milliequivalents/liter; alkalinity/ Cl^- ratio = meq/mole).

accentuates these patterns somewhat and reveals a possible temporal increase in alkalinity/ Cl^- in both winter and summer cases but particularly winter (Fig. 3C). *Upogebia* burrows have distinctly elevated alkalinity (Fig. 3B, 3D) relative to overlying waters.

Together with pH and Cl^- measurements titration alkalinity can be used to calculate the relative abundances of the various carbonate species (CO_2 , H_2CO_3 , HCO_3^- , CO_3^{2-}) in the burrow waters. The alkalinity contribution of boric acid was subtracted in each case to give carbonate alkalinity by assuming the apparent dissociation constants for boric acid of Lyman (1956) and the appropriate temperature ($T = 24^\circ\text{C}$)-salinity dependences compiled by Millero (1979). No corrections for nitrogen, phosphate, or silica species are necessary over the measured concentration and pH range (Hammond, 1973). After determining the carbonate alkalinity, the first and second apparent dissociation constants for carbonic acid (Mehrbach *et al.*, 1973; Millero, 1979) were used to estimate ΣCO_2 ($\text{CO}_2 + \text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-}$) and CO_2^* ($\text{CO}_2 + \text{H}_2\text{CO}_3$) (Table 1). The partial pressure of CO_2 (P_{CO_2}) was calculated at $T = 24^\circ\text{C}$ and for the salinity of each sample assuming the appropriate Henry's Law constant (Weiss, 1974). Calculated values of ΣCO_2 and P_{CO_2} are plotted in Figure 4.

Over the observed pH range alkalinity dominates the values of ΣCO_2 . These demonstrate that both burrow types have substantially more ΣCO_2 than overlying water. *Upogebia* burrows can have higher ΣCO_2 than *Onuphis* and larger departures from overlying water but in many cases the two are not greatly different. No distinct linear time trend in ΣCO_2 is observed although the highest values tend to occur after ~40 minutes exposure. In contrast, P_{CO_2} shows some large differences between the burrow types. Both burrow types are supersaturated at least $10\times$ the atmospheric

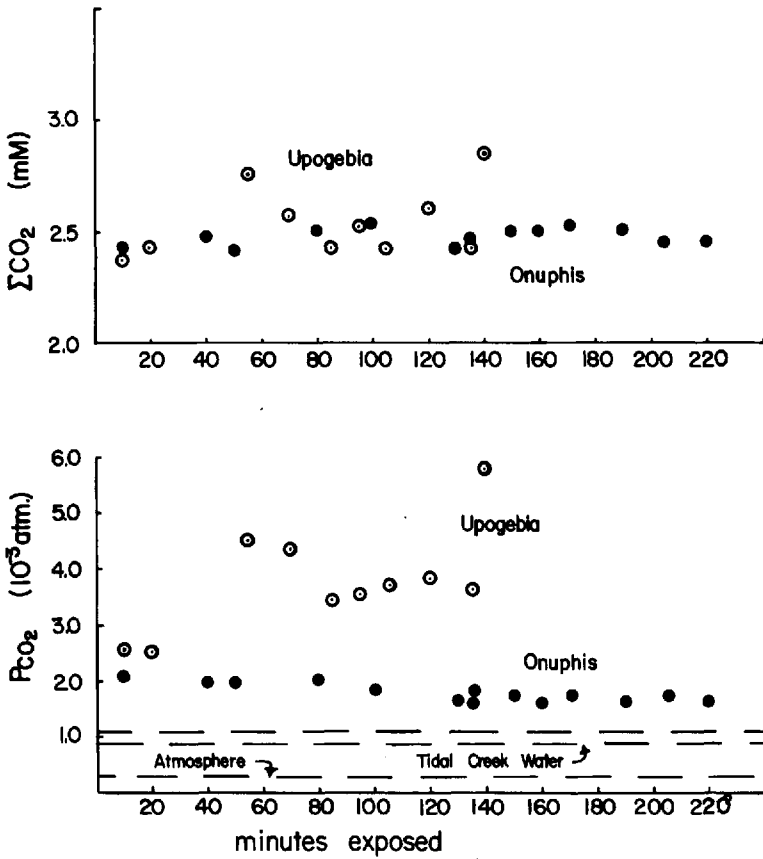


Figure 4. Calculated values of total CO₂(ΣCO₂) and P_{CO₂} in burrows during summer 1979. Solid circles = *Onuphis*; open circles with dot = *Upogebia*. Atmospheric and creek water P_{CO₂} ranges indicated as dashed lines. (mM = millimoles/liter).

value and 2–5× that of overlying water which is also supersaturated. The P_{CO₂} in *Upogebia* burrows is higher than in *Onuphis* and continues to increase with time to 20× atmospheric saturation while *Onuphis* P_{CO₂} either remains constant or drops slightly.

Both NH₄⁺ and I_T(I⁻ + IO₃⁻) concentrations build up in burrows of each species and increase regularly with time (Figs. 5, 6). *Upogebia* burrows reach significantly higher I_T concentrations than *Onuphis* but obtain similar NH₄⁺ levels in equivalent time periods. These constituents are both released from organic matter during decomposition. In contrast, HPO₄⁻, which is also released during decomposition, either has no significant elevation above overlying water values and decreases with time as in the case of *Onuphis*, or irregularly increases as in the case of *Upogebia* (Fig. 7).

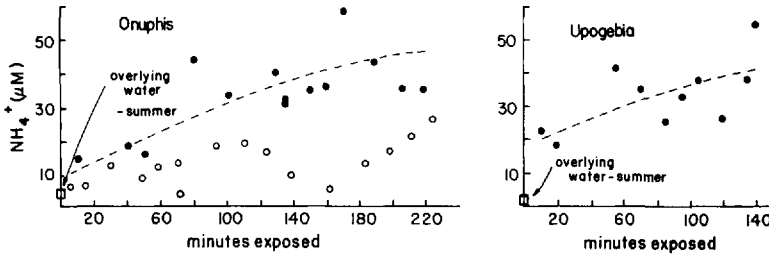


Figure 5. Dissolved ammonia in burrow waters. Solid circles = summer 1979; open circles = winter 1980; squares = overlying water. (μM = micromoles/liter).

Total $\text{NO}_2^- + \text{NO}_3^-$, referred to subsequently as NO_3^- , is initially higher than bottom water in both burrow types, unequivocally demonstrating the occurrence of nitrification within the burrows (Fig. 8). A regular decrease in NO_3^- takes place with time in the case of *Onuphis* implying net denitrification during the intertidal period. *Upogebia* burrow NO_3^- either remains elevated or decreases irregularly with time of exposure implying irregular dominance of nitrification or denitrification in individual burrows.

Mn^{++} and Fe^{++} , which may also be released by the reduction of Fe, Mn-oxides during decomposition and subsequently reoxidized, either show irregular increases relative to bottom water as in *Upogebia*, or, decreases or no changes for either burrow type (Figs. 9, 10).

Dissolved $\text{Si}(\text{OH})_4$ in both burrow types either rapidly increases to levels 25–100 μM above overlying water concentrations or may already be at some steady state value while the burrows are irrigated. $\text{Si}(\text{OH})_4$ remains at elevated levels during the intertidal or can decrease slightly as in the case of summer *Onuphis* samples (Fig. 11). Winter samples show a somewhat similar pattern but shifted to lower concentrations by about 25 μM . *Upogebia* burrow water has higher $\text{Si}(\text{OH})_4$ concentrations than *Onuphis* by as much as ~25–50 μM .

In *Onuphis* burrow water, total bacteria are the same or lower than overlying water

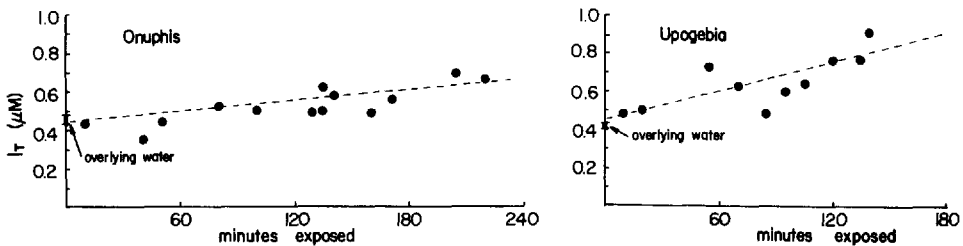


Figure 6. Total dissolved iodine ($\text{I}^- + \text{IO}_3^-$) in burrow waters during summer 1979. The least squares regression lines plotted, are for *Onuphis*: $y = 0.0009x + .434$ ($r = 0.77$, $N = 18$) and for *Upogebia*: $y = 0.0026x + .438$ ($r = .86$, $N = 13$).

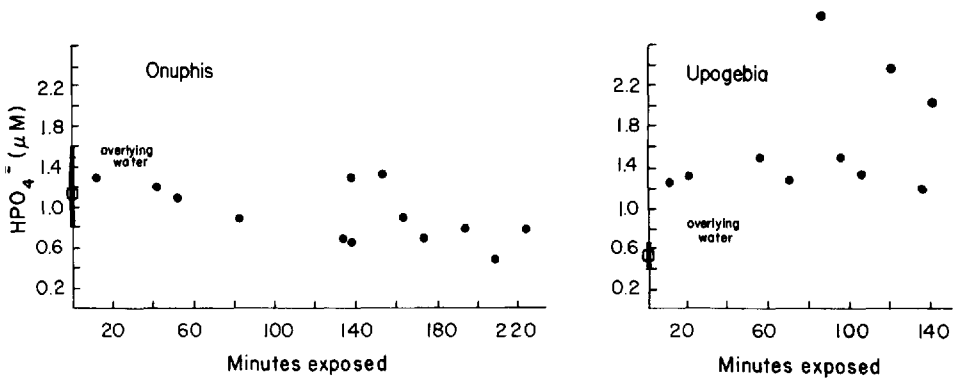


Figure 7. Dissolved phosphate in burrow and overlying water during summer 1979.

during summer and decrease with time. *Upogebia* burrow waters have irregular variations in the number of bacteria but unlike *Onuphis* can have counts twice that of overlying water (Fig. 12). The number of bacteria tends to be higher in general in *Upogebia* burrows than in *Onuphis* as well. Winter counts are lower for the most part than summer and apparently stay relatively constant with time. No significant difference between centrifuged and gravity-settled overlying water samples was found. Approximately 50% of the stained bacteria in all cases appeared to be unattached to particles.

b. Adsorption experiments. *Onuphis* polysaccharide tube linings adsorbed or desorbed significant concentrations of NH_4^+ , HPO_4^{2-} , and $\text{Si}(\text{OH})_4$ from contacting solutions. Adsorption behavior is apparently linear over the concentration range investigated and temperature of the experiments ($T = 25^\circ\text{C}$). Initial experiments using only $\text{Si}(\text{OH})_4$ solutions in distilled water ($\text{pH} = 5.8$) showed that the adsorption isotherms obtained after 1 hr or 4 days were different and therefore adsorption is moderately time dependent (Fig. 13). Subsequent adsorption experiments in sea water

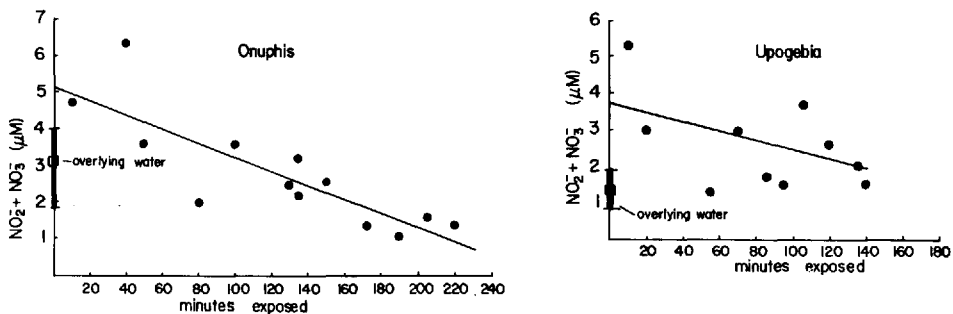


Figure 8. Nitrite and Nitrate in burrow and overlying water; summer 1979.

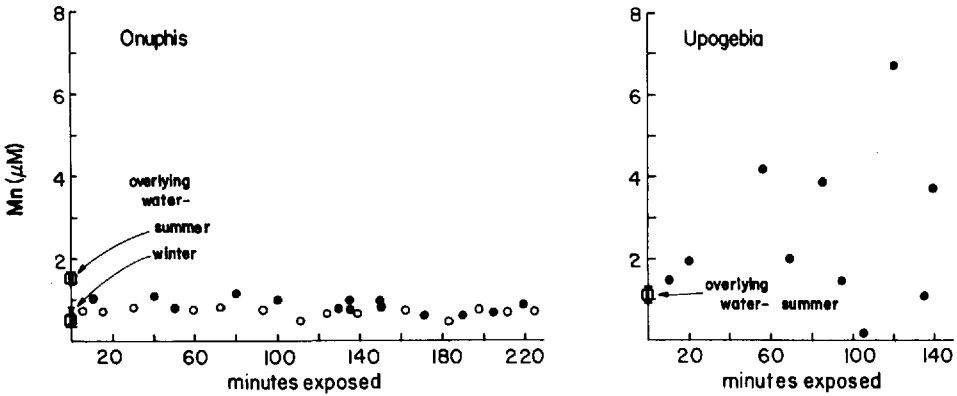


Figure 9. Dissolved manganese in overlying and burrow waters. Solid circles = summer 1979; open circles = winter 1980; squares = overlying water.

standards were done over a period of 2–2.5 hrs to approximately correspond to the intertidal incubation times.

Four sets of adsorption experiments were done with sea water standards. Three of these used sections of *Onuphis* tubes with variable quantities of the agglutinated sand layer removed and the fourth used only the sand fraction (~0.6 g aliquots) from the flat. All three solutes, whether positively, negatively, or neutrally charged, were adsorbed. Control solutions did not change relative to standards. These experiments showed that the quantity of solute adsorbed or desorbed per total mass of material depended strongly on the relative abundance of sand and organic tube lining present. Results from only three of the four runs are plotted for clarity in Figure 14. These demonstrate that the agglutinated sand layer has a lower affinity for solute adsorption relative to the organic tube lining and acts as a diluent to reduce the slope of the isotherm. Normalization of the quantity of adsorbed-desorbed solute to the mass of organic C present rather than total mass produces linear isotherms when the results of the three experiments with tube sections are plotted together (Fig. 15). The NH_4^+ analyses on one run were contaminated and could not be used.

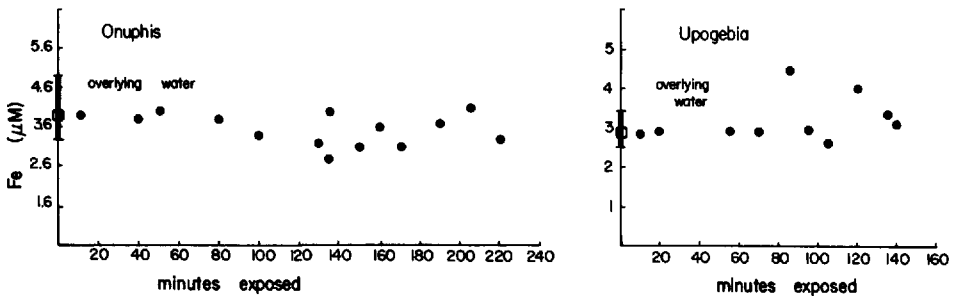


Figure 10. Dissolved iron in overlying and burrow waters; summer, 1979.

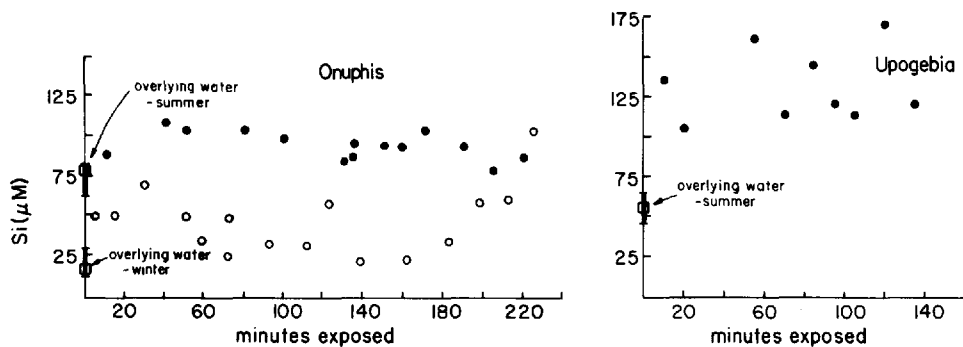


Figure 11. Dissolved silica in overlying and burrow waters. Solid circles = summer 1979; open circles = winter 1980; squares = overlying water.

The mean quantity of organic carbon per length of tube was calculated as 0.227 ± 0.067 mgC/cm tube length ($N = 30$) or 0.227 ± 0.049 ($N = 28$) if two outlying analyses are ignored. The average radius of the tubes below the distal tapered section both in the experiments and on Cooks Creek flat is $\sim 0.212 \pm 0.021$ cm ($N = 65$). Total tube wall thickness including the agglutinated sand layer averaged 223 ± 31 μm ($N = 10$). Along with the isotherms of Figure 14, these quantities allow calculation of adsorption relative to organic C, tube length, tube wall volume, or tube surface area.

5. Discussion

a. Reactions occurring in the burrows. Both the magnitude and time dependence of solute concentrations in the two burrow types imply similarities in the general kinds of biogeochemical and abiotic reactions taking place in each case but possibly

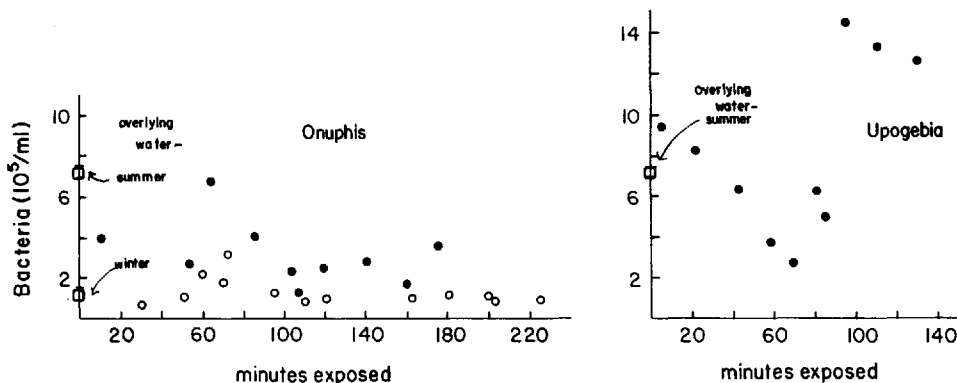


Figure 12. Numbers of bacteria in overlying and burrow waters. Solid circles = summer 1979; open circles = winter 1980; squares = overlying water.

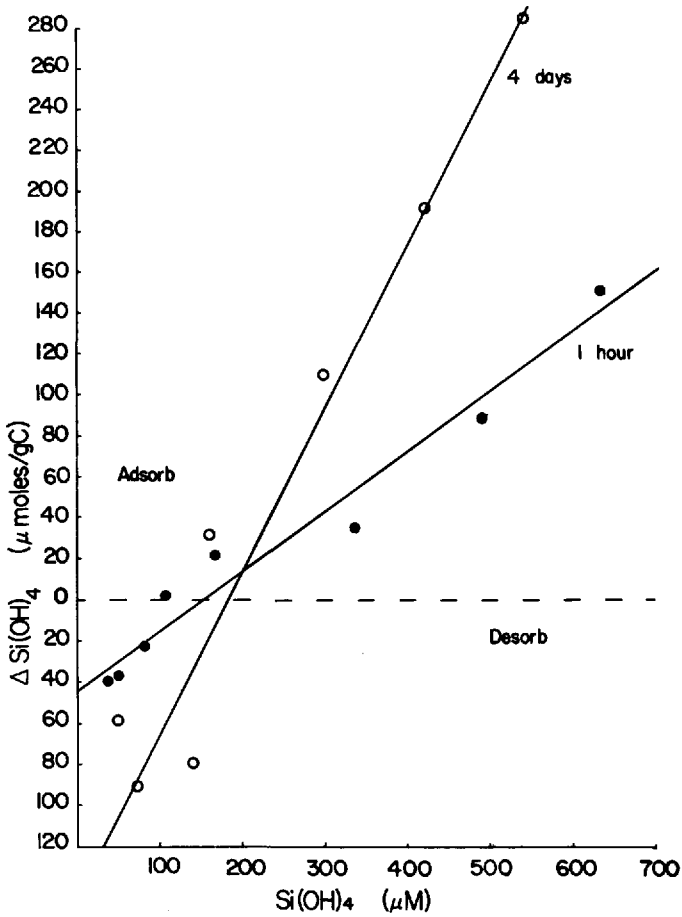
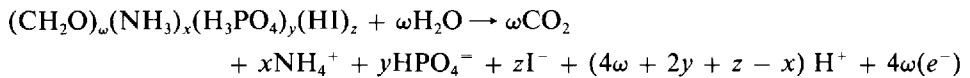


Figure 13. Adsorbed or desorbed silica on *Onuphis* tubes per gram organic carbon versus dissolved silica in distilled water standards ($\mu\text{M} = \mu\text{moles/liter}$). Solid circles = 1 hr reaction; open circles = 4 days reaction. $T = 25^\circ\text{C}$.

substantial differences in their relative importance. In both *Onuphis* and *Upogebia* burrows the buildup of some of the products of organic matter decomposition resulting from heterotrophic metabolism is evident. Idealized representations of the major oxidation-reduction half reactions involved are (modified after Richards, 1965; Stumm and Morgan, 1970):

Carbon oxidation—organic matter hydrolysis (1)



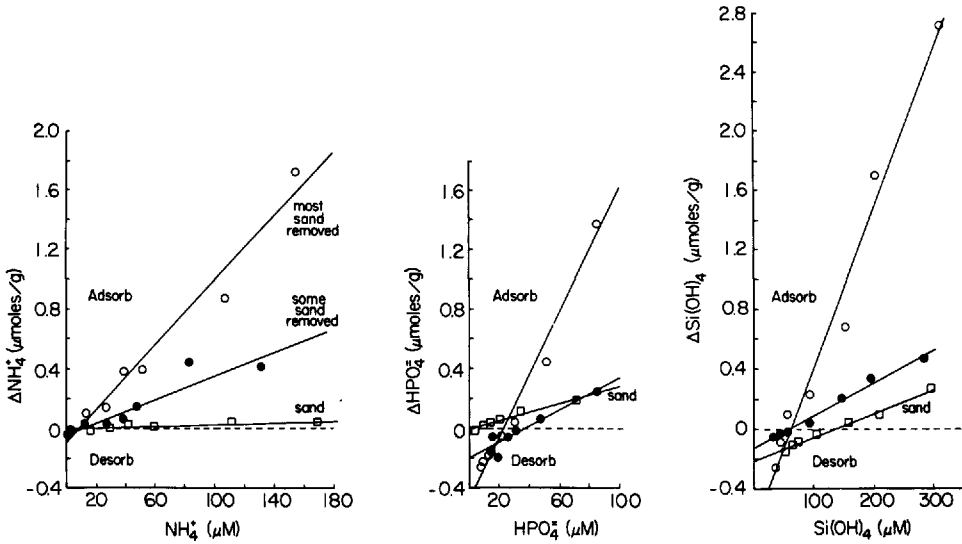


Figure 14. NH_4^+ , HPO_4^- , and Si(OH)_4 adsorbed per gram *Onuphis* tube or sand as function of concentration in standard solutions made up in sea water. Variable amounts of agglutinated sand layer were removed from tubes in the two cases shown. Sand acts as a deluent.

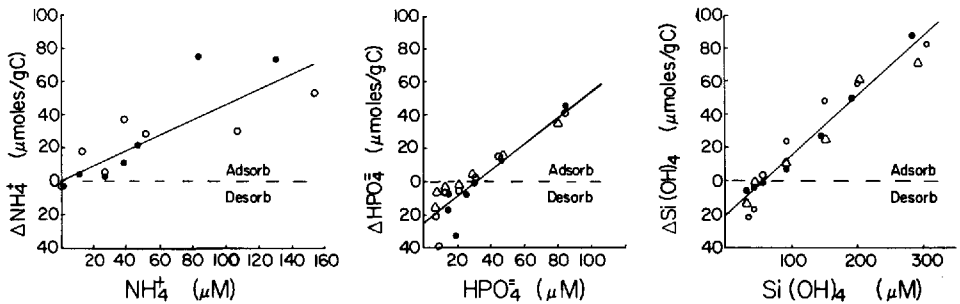
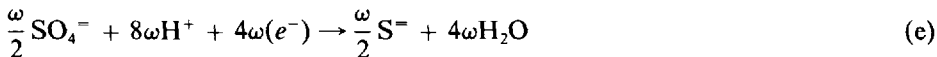
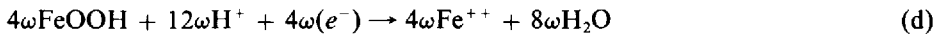
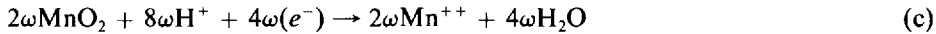
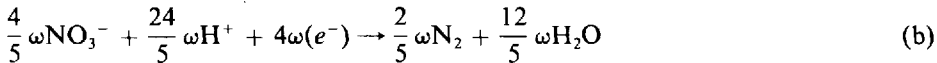


Figure 15. NH_4^+ , HPO_4^- , and Si(OH)_4 adsorbed per gram organic carbon in *Onuphis* tube sections as function of concentration in standard solutions made up in sea water. Results of three separate experiments are plotted for HPO_4^- and Si(OH)_4 and two runs for NH_4^+ . The open and filled circles represent the same experiments plotted relative to total mass in Figure 14. The least squares regression lines plotted are for NH_4^+ : $y = 0.438x + 2.64$ ($r = 0.81$, $N = 14$); for HPO_4^- : $y = 0.785x - 24.6$ ($r = 0.91$, $N = 21$); and for Si(OH)_4 : $0.365x - 21.4$ ($r = 0.97$, $N = 21$); where x is solution concentration in μM and y is adsorbed solute in $\mu\text{moles/gC}$.

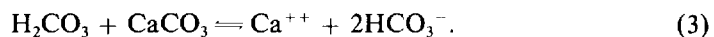
Electron acceptor reduction (2)



The average oxidation state of decomposing organic carbon is assumed for simplicity to be that of carbohydrate. The stoichiometry of net decomposition, $\omega/x/y/z$, for marine planktonic material tends over all to a C/N/P/I ratio of $\sim 106/16/1/0.011$ (Redfield, 1934; Richards, 1965; Elderfield and Truesdale, 1980). Deviations from this ratio may occur at various points in decomposition as different classes of compounds are utilized preferentially. Such deviation is often characterized by relative enrichments of N, P, and I during initial decomposition compared with later stages (Grill and Richards, 1964; Sholkovitz, 1973; Skopintsev, 1981; Ullman and Aller, 1983). The half reactions 2a, b, c, d, and e are known to be mediated by bacteria in a temporal succession following the relative order of the free energy change during reduction: $\text{O}_2 > \text{NO}_3 \gtrsim \text{Mn} > \text{Fe} > \text{SO}_4$ (e.g. Claypool and Kaplan, 1974; Froelich *et al.*, 1979).

Differences in the biogeochemical microenvironments of *Onuphis* and *Upogebia* burrows can be elucidated in part by examining the relative buildup or apparent stoichiometry of decomposition products in each case. Figure 16 demonstrates that the net N/C ratio of decomposition products calculated from $\text{NH}_4^+/\Sigma\text{CO}_2$ analyses is ~ 0.051 in *Upogebia* burrows while that in *Onuphis* burrows is ~ 0.17 , close to the 0.15 value expected for average marine organic matter. No correction for NH_4^+ adsorption is made at this point but it is unlikely to change the relative ratios found in the two burrow types. Because the initial fluxes into burrows should be close to those supported by steady state production rates in surrounding sediment, differences in solute diffusion coefficients should have a minimal effect on the calculated ratios. Addition of the measured $\text{NO}_2^- + \text{NO}_3^-$ concentration excesses above overlying water to the mineralized N fraction does not substantially alter relative differences.

The dissolution of CaCO_3 in the burrow walls could result in diffusive addition to burrow waters of ΣCO_2 (mostly as HCO_3^-) without corresponding dissolved N (Emerson *et al.*, 1980). This would result in a decrease in the apparent N/C ratio. Dissolution is represented by the equation:



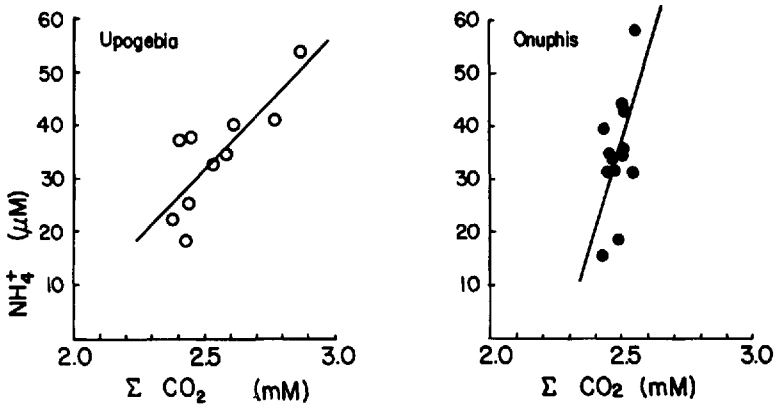
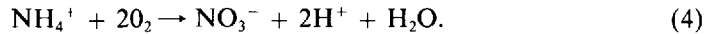


Figure 16. Dissolved NH_4^+ relative to ΣCO_2 in *Upogebia* and *Onuphis* burrows. The lines plotted are for C/N ratios of 19.6 and 5.8 mole/mole respectively.

The saturation states of burrow water with respect to both aragonite and calcite were calculated assuming a $\text{Ca}^{++}/\text{Cl}^-$ of 18.8 mmole/mole, the previously calculated carbonate species distribution, and the apparent solubility constants, K'_{sp} , of Ingle *et al.* (1973) at the appropriate temperature and salinity (Millero, 1979). The mean ratio $\Lambda = [\text{Ca}^{++}][\text{CO}_3^{--}]/K'_{sp}$ is $1.67 \pm .14$, $1.2 \pm .13$, and $0.60 \pm .10$ for aragonite in overlying water, *Onuphis* burrows, and *Upogebia* burrows respectively. The corresponding Λ 's for calcite are $2.6 \pm .22$, $1.8 \pm .19$, and $0.91 \pm .15$. *Upogebia* burrow waters are therefore substantially undersaturated with respect to both aragonite and calcite while overlying waters and *Onuphis* burrow waters are supersaturated. This means that part of the carbon enrichment relative to N in *Upogebia* burrows could be provided by calcium carbonate dissolution during easing of undersaturation; however, the fact that pH continues to drop during the addition of ΣCO_2 (Fig. 2) and additional considerations discussed later indicate that other factors are probably responsible.

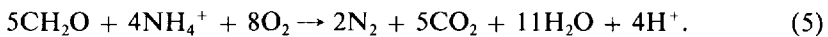
In contrast to the apparent differences in the N/C decomposition ratio, the I/C ratio of solutes entering both burrow types is nearly the same. This ratio is $0.67 \mu\text{mole I/mmole C}$ for *Upogebia* as obtained from a plot of I_T versus ΣCO_2 and is $0.62 \mu\text{mole/mmole}$ for *Onuphis*, calculated from the difference between the mean $I_T/\Sigma\text{CO}_2$ ratios in overlying water ($0.467/2.368$) and burrow waters ($0.538/2.482$). This latter calculation was necessary because of the small range in both I_T and ΣCO_2 concentrations. The I/C ratio measured from anoxic decomposition experiments in marine mud taken from a nearby estuarine area is $0.6 \pm 0.1 \mu\text{mole/mmole}$ (Ullman and Aller, 1983) and a ratio of 0.48 is reported for Narragansett Bay sediments (Elderfield *et al.*, 1981a). The burrow I/C ratios are therefore consistent with other reported early decomposition values. It is, of course, possible that I^- or IO_3^- is lost from solution preferentially in either *Onuphis* or *Upogebia* burrows so that agreement between ratios is more apparent than real.

The similarity between the I/C stoichiometry calculated for both burrow types as well as a N/C ratio close to the theoretical average in the *Onuphis* burrows implies that comparable organic material is being broken down in each case and that the reason for low N/C ratios in *Upogebia* burrows is not necessarily due to Ca carbonate dissolution but may be due to the conversion at some point of remineralized N to a form other than NO_2^- , NO_3^- , or NH_4^+ . One explanation for these differences is that nitrification and denitrification rates (Eq. 1 and Eq. 2b) may vary substantially between each burrow type. Nitrification occurs in the two ecologically coupled steps of NH_4^+ oxidation to nitrite followed by nitrite oxidation to give the overall reaction:



The molar ratio of CO_2 fixed to NH_4^+ oxidized in these chemoautotrophic reactions varies with microbial growth state, chemical environment history, and O_2 partial pressure (Gundersen, 1966; Carlucci and McNally, 1969; Van Gool *et al.*, 1971). Highest carbon fixation and N-oxidation occur at low P_{O_2} with substantial oxidation rates at O_2 concentrations of just a few μM (Gundersen *et al.*, 1966; Carlucci and McNally, 1969). The observation of high oxidation rates at low P_{O_2} is critical in the present instance because burrows are known to have low O_2 contents during intertidal periods (Jones, 1955; Petersen and Johansen, 1967; Thompson and Pritchard, 1969). The molar C fixed/N oxidized ratios are ~ 0.06 – 0.14 for NH_4^+ oxidation and ~ 0.01 – 0.02 for nitrite oxidation to give typical ratios of ~ 0.12 for the overall reaction equation (4) (Billen, 1976; Watson and Waterbury, 1971; Van Gool *et al.*, 1971). This means that because of the relative abundance of NH_4^+ and ΣCO_2 , nitrification may influence dissolved N patterns substantially without easily detectable ΣCO_2 change.

The coupling of denitrification and nitrification gives the overall reaction (ignoring CO_2 fixation):



This means that although changes in ΣCO_2 may be analytically hard to detect, these reactions should result in readily detectable lower pH and higher P_{CO_2} (Gundersen and Mountain, 1973; Brewer and Goldman, 1976). The pH of *Upogebia* burrows is much lower than those of *Onuphis* and P_{CO_2} is higher. These observations, together with the observed N/C and I/C stoichiometries and the fact that carbonate dissolution should raise not lower pH with ΣCO_2 increase, imply that *Upogebia* burrows are sites of intense nitrification-denitrification compared with those of *Onuphis*. The particular nitrate concentration balance achieved is not greatly different, however. Consideration of the required relative reaction rates in a later section indicate that they are within naturally observed ranges. Species specific differences in burrow wall nitrification-denitrification rates for several infaunal species have been demonstrated in laboratory aquaria, lending further support to the likelihood of the present interpretation (Henriksen *et al.*, 1982).

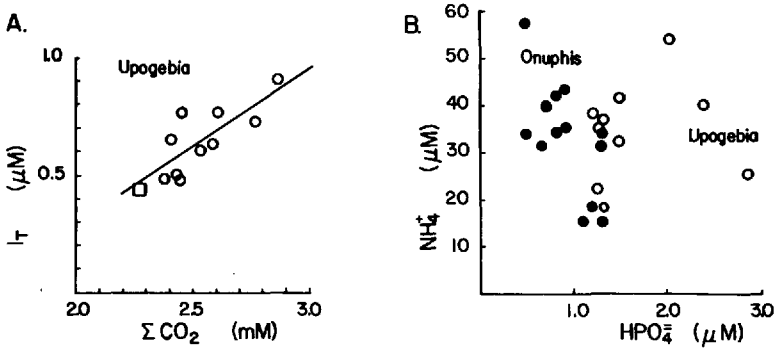


Figure 17. (A) Total dissolved iodine relative to ΣCO_2 in *Upogebia* burrows and overlying water (square). The I/C ratio of the line plotted is 0.67 $\mu\text{mole}/\text{mmole}$. (B) Dissolved NH_4^+ relative to HPO_4^- in *Onuphis* (●) and *Upogebia* (○) burrow waters (summer, 1979). No regular relation occurs.

Despite the net release into burrows of decomposition products like NH_4^+ and I_T , HPO_4^- concentrations either decrease slightly as in the case of *Onuphis* or increase irregularly above bottom water values as in *Upogebia* burrows (Fig. 7). There is no regular correlation of NH_4^+ , for example, with HPO_4^- in either burrow type (Fig. 17B). Based on the idealized decomposition ratio for marine plankton an increase of $\geq 3 \mu\text{M}$ HPO_4^- should accompany the $\sim 50 \mu\text{M}$ increase in NH_4^+ . Part of the lack of HPO_4^- increase is almost certainly due to the greater adsorption affinity for HPO_4^- than NH_4^+ by *Onuphis* tube linings (Fig. 15) and probably the mucus Fe-oxide laden inner burrow wall of *Upogebia* as well. Adsorption will reduce or buffer the concentration excursions of adsorbed-desorbed constituents (see later discussion).

Because of the obvious occurrence of denitrification in *Onuphis* and *Upogebia* burrows (Fig. 8), it is likely that Mn reduction (Eq. 2c) also takes place in close proximity. High Mn^{++} concentrations ($\sim 10\text{--}50 \mu\text{M}$, unpublished data) measured in pore water within a centimeter radius of both *Onuphis* and *Upogebia* burrows support this expectation. *Upogebia* burrows show large excursions in Mn^{++} concentrations; there are both large increases, implying Mn reduction, and decreases, indicating loss by adsorption or possibly microbially mediated oxidation (Rosson and Neelson, 1982). This variability in behavior is consistent with the previous discussion of nitrification-denitrification which implied intense, heterogeneous microbial activity in the burrow wall.

Iron shows several instances of modest increase in *Upogebia* burrows, indicating net Fe-reduction (Eq. 2d) or possibly Fe-sulfide oxidation. We argued in a previous paper that chemoautotrophic Fe-sulfide oxidation takes place in *Amphitrite ornata* burrow walls resulting in elevated Fe^{++} and microacid mine drainage-like conditions within the burrows of that species (Aller and Yingst, 1978). No evidence for extensive sulfide oxidation is found here, either from $\text{SO}_4^-/\text{Cl}^-$, Alkalinity/ Cl^- , or Fe^{++} concentration

relationships. This does not mean it does not occur, it almost certainly does, but it does not dominate the observed burrow water properties. The fact that Mn^{++} , HPO_4^+ , and possibly Fe also, decrease in *Onuphis* burrows over the tidal period implies the possible formation in the burrows of a Mn, Fe-phosphate, perhaps nucleated or catalyzed by the adsorption properties of the tube lining.

The apparent rapid rise and leveling off of silica concentrations in both *Onuphis* and *Upogebia* burrows can be explained in part by a decrease in the diffusive flux as burrow water approaches pore water in concentration (Fig. 11). Pore water concentrations range from $\sim 400\text{--}500 \mu\text{M}$ (unpublished data) in the immediate vicinity of burrows, however, so that burrow water concentrations should have continued to increase if diffusive flux alone were the controlling factor. The apparent constancy or even slight decrease in $Si(OH)_4$ concentrations in *Onuphis* burrows may, like Mn, Fe, and HPO_4^- , be related in part to adsorption by the tube wall and surrounding sediment (Figs. 11, 13–15) or precipitation of a new authigenic mineral phase. *Upogebia* burrow wall mucus (see Thompson, 1972) may also play a similar adsorption or nucleation role but less dominate in the sense of lowering the concentration of silica. The strong affinity of dissolved $Si(OH)_4$ for the *Onuphis* tube lining, and possibly the organic cement of the *Upogebia* burrow, may help explain the observation of preferentially silicified burrow structures in the fossil record.

b. Reaction and flux rates. If, as has been implicitly assumed in the previous discussion, each burrow of a general type behaves identically to another, then the time series incubation provided by the ebb tidal period can be used to place limits on reaction rates or fluxes of dissolved material into and out of the burrows (Aller and Yingst, 1978). The time rate of change of burrow water concentration during the ebb tidal or *no irrigation period* for a particular solute is given by:

$$\frac{\partial C_i}{\partial t} = \frac{A \cdot J_i}{V} + R_i = \frac{2J_i}{r} + R_i \quad (6)$$

where: C_i = burrow water concentration of solute i

t = time

J_i = net flux of solute i from/into burrow wall (mass/cm²/time)

A = area of burrow wall

V = volume of burrow core

r = radius of burrow (assumed to be perfect cylinder)

R_i = net reactions or additional source/sinks in burrow water affecting solute i

When a burrow is being irrigated, the steady state solute concentration difference between water in the burrow and overlying water is related to the irrigation rate, solute

flux from/into surrounding sediment, and additional reactions by the relation:

$$\begin{aligned} \frac{v}{V}(C_{o_i} - C_{T_i}) &= \frac{v}{V}(\Delta C_i) = \frac{v}{\pi r^2 L}(\Delta C_i) \\ &= \frac{2J_i}{r} + R_i \end{aligned} \quad (7)$$

where: C_{o_i} = steady state burrow water concentration of solute i or concentration at $t = 0$.

C_{T_i} = overlying water concentration of solute i

v = irrigation rate (water volume/time)

L = burrow length

If it is assumed that either the concentration in the first sampled burrow in a time series is a good estimate of C_{o_i} , or that C_{o_i} can be estimated by extrapolation of C_i to $t = 0$ from the time series data, then it is possible to estimate two of the variables J_i , R_i , or v if one is known and burrow size is also known. In general, average burrow radius is known but length is not so that only the ratio v/L can be calculated. Because this ratio is constant for all solutes, if it can be estimated in any single case it can be applied to all.

NH_4^+ is the only solute in each burrow type having both an initial concentration different than overlying water and a well-defined change in concentration with time. The average radius of *Onuphis* burrows from which water was extracted was 0.21 ± 0.03 cm and the average radius of *Upogebia* burrows was 0.65 ± 0.15 . These radii and the estimated C_o , C_T , and $\partial C/\partial t$ from the curve fits in Figure 5 can be used together with Eqs. (6) and (7) to calculate v/L (Table 2). The calculated values are $0.014 \text{ cm}^2/\text{min}$ for *Onuphis* and $0.029 \text{ cm}^2/\text{min}$ for *Upogebia*. If, as a check, reasonable burrow lengths of ~ 70 cm ($V \sim 9.7$ ml) and ~ 150 cm ($V \sim 200$ ml, based on removal of burrow water) are assumed for *Onuphis* and *Upogebia* respectively, the resulting irrigation rates are ~ 60 cc/hr and ~ 174 cc/hr. These are low for suspension-feeding organisms but are of comparable magnitude to the irrigation rates of many other macroinfauna. The *Onuphis* estimate in particular is close to the reported value of ~ 68 ml/hr for the related form *Diopatra cuprea* (Mangum et al., 1968).

Assuming either the v/L value for *Onuphis* or *Upogebia* and measured initial or extrapolated ΔC_i , or the measured $(\partial C_i/\partial t)_{t=0}$, net flux estimates were made for NO_3^- (nitrification), NO_3^- (denitrification), I_T , CO_2^* ($= \text{CO}_2 + \text{H}_2\text{CO}_3$), ΣCO_2 , and Si. These calculations are listed in Table 2. The reaction rate term R_i is ignored in all cases except for NH_4^+ and NO_3^- (denitrification) where a third flux was calculated by adding both the nitrification and denitrification fluxes to the original estimate of net NH_4^+ flux or the denitrification flux to the NO_3^- (nitrification) rate. The individual kinds of calculations are differentiated in Table 2 as $J_1 = (r/2)(\partial C_i/\partial t)$, (net flux during ebb tide when no irrigation occurs), $J_2 = (v/L2\pi r)(\Delta C_i)$, (net flux during irrigation period), which use Eqs. (6) and (7) respectively, and J_3 which are the

Table 2. Reaction and flux rates of dissolved materials into and out of burrows of *Onuphis jenneri* and *Upogebia affinis*.

	C_o	C_i	ΔC	$\partial C/\partial t$	J_1	J_2	J_3
<i>Onuphis</i>	μM	μM	μM	$\mu\text{M}/\text{min}$	nmoles/ $\text{cm}^2 \text{min}$	nmoles/ $\text{cm}^2 \text{min}$	nmoles/ $\text{cm}^2 \text{min}$
NH_4^+							
Summer	8.7	5.2	3.5	0.36	0.038	0.038	0.063
Winter				0.051	0.005		
NO_3^-	5.2	3.1	2.1			0.023	0.025
(Nitrification)							
NO_3^-				-0.019	-0.002		
(Denitrification)							
I_t				0.0013	0.00014		
CO_2^*	54	31	23			0.25	
ΣCO_2	2434	2368	66			0.72	
$\text{Si}(\text{OH})_2$							
Summer	94.8 ± 8.6	75.6 ± 8.5	19.2			0.21	
Winter	48 ± 22	17 ± 11	31				
<i>Upogebia</i>							
NH_4^+	16.9	2.1	14.8	0.32	0.10	0.10	0.12
NO_3^-	3.7	1.4	2.3			0.016	0.02
(Nitrification)							
NO_3^-				-0.012	-0.004		
(Denitrification)							
I_t				0.0024	0.00079		
CO_2^*	81.8	33.4	48	0.389	0.13	0.34	
ΣCO_2	2405	2267	138			0.97	
$\text{Si}(\text{OH})_4$	131 ± 22	55 ± 7.5	76			0.53	

J_1 = net flux based on rate of change of burrow water composition during low tide (no irrigation period)

J_2 = net flux based on initial concentration differences between burrow and overlying water (irrigation period)

J_3 = partially corrected fluxes for nitrification-denitrification (minimum correction)

partially corrected net NH_4^+ and NO_3^- (nitrification) fluxes. J_2 estimates should be relatively accurate estimates of net fluxes leaving burrows while J_1 estimates may be strongly influenced by transient state reactions or conditions such as adsorption or O_2 depletion, that is, R_i in Eqs. (6) and (7) may not be the same. Because of the inability to evaluate R_i either wholly or in part, in most cases these fluxes are likely to be minima.

Taken at face value, the calculated fluxes relative to burrow wall area are within typical ranges reported for nearshore surface sediments: ~ 1 – 2 mmoles/ m^2/day for NH_4^+ , 0.3 – 0.4 mmoles/ m^2/day nitrification, 30 – 60 $\mu\text{moles}/\text{m}^2/\text{day}$ denitrification, 2 – 11 $\mu\text{moles}/\text{m}^2/\text{day}$ I_T , 10 – 14 mmoles/ m^2/day ΣCO_2 , and 3 – 8 mmoles/ m^2/day Si (Nixon *et al.*, 1976; Seitzinger *et al.*, 1980; Zeitzschel, 1980; Aller and Benninger, 1981; Ullman and Aller, 1980; Elderfield *et al.*, 1981b). All calculations made relative

to burrow wall area assume that excretion by the macrofaunal inhabitant is comparatively insignificant during the intertidal period due to reduced or resting metabolism at low O_2 levels (Thompson and Pritchard, 1969; Mangum and Burnett, 1975). If this assumption is incorrect, flux estimates from surrounding sediment generally decrease depending on the particular solute involved (Henriksen *et al.*, 1982).

In general, the estimated fluxes are consistently higher in *Upogebia* burrows than *Onuphis* suggesting, along with higher levels of bacteria at $t = 0$ (Fig. 12), that *Upogebia* burrows may be somewhat more microbially active sites than the lined tubes of *Onuphis*. Lower bacteria levels in *Onuphis* burrow water may also reflect differences in feeding activity or inhibition of microbial growth by enzymes in the tube lining (Zottoli and Carriker, 1974). Based on these calculations, the proportion of the NH_4^+ flux which is nitrified is apparently ~20–50%, similar to the percentages reported by Seitzinger *et al.* (1980) for Narragansett Bay surface sediment. Because these calculations are made on the basis of rate differences, however, and because reactions such as adsorption are not entirely taken into account, all rates are suspect in an absolute sense. For example, nitrification-denitrification rates in *Upogebia* burrows could be 3–4 \times the estimated value without being in serious conflict with either the estimated CO_2^* flux or relative $NH_4^+ / \Sigma CO_2$ fluxes. In fact the previous stoichiometric considerations require such an increase.

As just implied, in principle the ratios between steady state fluxes can be used as a measure of decomposition stoichiometry. The calculated $N / \Sigma CO_2$ flux ratios (from Table 2) are in fact quite reasonable at ~0.12 for *Upogebia* and 0.09 for *Onuphis*; however, because of the large uncertainties and various assumptions involved in individual fluxes further calculation of ratios seems unwarranted and probably misleading.

c. Burrow lining controls on burrow water composition. The adsorption experiments and the time dependence of burrow water solute concentrations imply that tube linings and organic enriched burrow walls have substantial influence on burrow chemistry. A diffusion-reaction model can be constructed to quantitatively examine this influence. The geometry of diffusion around a burrow is idealized as shown in Figure 18A. When the tide recedes, irrigation stops and dissolved constituents begin to diffuse into or out of surrounding sediment through a burrow lining out of or into what is now a small, fixed reservoir of burrow water. This reservoir is cylindrical in shape. Rather than solving this problem exactly in cylindrical coordinates, a one-dimensional analogue geometry is assumed which incorporates many of the basic features of the problem. This simplified analogue, which takes advantage of the burrow symmetry across a plane that includes the burrow axis, is shown in Figure 18B. It consists of a well-mixed water reservoir of fixed volume, V (corresponding to one half the burrow), adjacent to a two layer body; one layer corresponds to the inner burrow lining (thickness 0 to L_1) and the second to surrounding sediment (thickness L_1 to L_2).

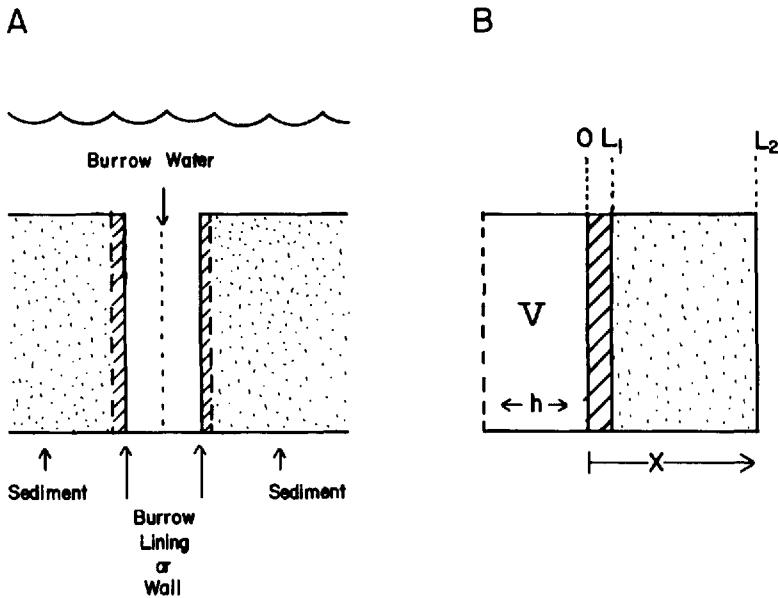


Figure 18. (A) Cross-section of ideal burrow showing burrow lining, surrounding sediment, overlying water, and burrow water. (B) Simplified diffusion geometry used to represent the burrow water and surrounding layers in the diffusion-reaction model for burrow water composition. After the tide recedes, the burrow water volume, $2V$, becomes finite. The model geometry corresponds to one half of the ideal burrow of (A) as measured from the burrow axis, with an additional simplification of the natural cylindrical symmetry to a one-dimensional cartesian space coordinate, x , which is positive away from the inner surface of the burrow lining.

In setting up the model equations to be solved it is assumed that no reactions other than adsorption take place in either the burrow water or lining and that only zeroth order reactions typical of certain kinds of metabolic activity are allowed in surrounding sediment. Pore water advection perpendicular to the burrow axis is ignored and solute concentrations are assumed to go through a maximum or minimum at L_2 , where L_2 is half the distance between adjacent burrows. The concentration profile of a dissolved constituent in both the burrow lining and surrounding sediment when V becomes finite (irrigation ceases) is taken to be parabolic (measured perpendicular to the burrow). The appropriate diffusion-reaction equations with layer 1 corresponding to tube lining and layer 2 to surrounding sediment are:

Layer 1 (burrow lining)

$$\frac{\partial C_1}{\partial t} = \frac{D_1}{1 + K_1} \left(\frac{\partial^2 C}{\partial x^2} \right) \quad (8a)$$

Layer 2 (surrounding sediment)

$$\frac{\partial C_2}{\partial t} = \frac{D_2}{1 + K_2} \left(\frac{\partial^2 C_2}{\partial x^2} \right) + \frac{R}{1 + K_2} \quad (\text{b})$$

Water Reservoir (inside burrow)

$$\frac{\partial C_T}{\partial t} = -\frac{\phi_1}{h} D_1 \left(\frac{\partial C_1}{\partial x} \right) \quad (\text{c})$$

With initial and boundary conditions:

$$t = 0; x \geq 0, C = C_o + a_1x + a_2x^2 \quad (\text{9a})$$

$$C_T = C_o \quad (\text{b})$$

$$t \geq 0; x = 0, C_T = C_1 \quad (\text{c})$$

$$x = L_1, C_1 = C_2 \quad (\text{d})$$

$$\phi_1 D_1 \frac{\partial C_1}{\partial x} = \phi_2 D_2 \frac{\partial C_2}{\partial x} \quad (\text{e})$$

$$x = L_2, \frac{\partial C_2}{\partial x} = 0 \quad (\text{f})$$

Where:

C_T = solute concentration in burrow water

C_o = initial concentration in burrow water

C_1 = solute concentration in tube lining

C_2 = solute concentration in surrounding sediment

x = space coordinate, positive away from burrow wall into sediment

t = time

R = constant reaction rate (zeroth order)

h = ratio of burrow water volume to area of burrow wall

K_1, K_2 = linear adsorption coefficients in layer 1 and 2 (see Berner, 1976)

D_1, D_2 = bulk sediment diffusion coefficients in layer 1 and 2

ϕ_1, ϕ_2 = porosity of layer 1 and 2

L_1, L_2 = thickness measured from $x = 0$ of layer 1 and 2

a_1, a_2 = constants; $a_1 = -2a_2L_2$ to satisfy boundary condition at L_2 .

Only the burrow water concentration C_T is of interest here. The solution for C_T is given in the Appendix.

The model will be evaluated using NH_4^+ to illustrate the principles involved. Three kinds of model cases are considered here, one where K_1 the adsorption coefficient of the burrow wall is allowed to vary, another where D_1 the diffusion coefficient in the burrow is varied, and the third in which h , the burrow volume/wall area is changed. In the first

two cases the remaining model variables are fixed initially at the following values:

$$\begin{aligned} h &= 0.1 \text{ cm}; C_o = 5 \mu\text{M}; R = 0.028 \mu\text{M}/\text{min}; L_1 = 0.02 \text{ cm}; \\ L_2 &= 4.5 \text{ cm}; \phi_1 = 0.711; \phi_2 = 0.502; D_2 = 0.000582 \text{ cm}^2/\text{min}; \\ K_2 &= 0.79; a_1 = 220.7 \mu\text{M}/\text{cm}; a_2 = -24.5 \mu\text{M}/\text{cm}. \end{aligned}$$

These were chosen so that (1) h corresponds to an average *Onuphis* burrow of radius 0.21 cm, (2) R would supply the estimated flux at steady state ($V, t \rightarrow \infty$) of 0.063 nmoles/cm²/min listed in Table 2, (3) K_2 is calculated relative to pore water volume ($\mu\text{mole adsorbed NH}_4^+/\text{volume pore water}$)/($\mu\text{mole dissolved NH}_4^+/\text{volume pore water}$) (unpublished data), (4) L_1 corresponds to the average tube wall thickness, (5) L_2 corresponds to half the distance between burrows when the natural abundance of a uniformly dispersed population is $\sim 160/\text{m}^2$, and (6) a_1 and a_2 were chosen to give an average concentration of 336 μM in layer 2 corresponding to that measured around *Onuphis* burrows in the field (unpublished). The porosity ϕ_2 was estimated from the average Cooks Creek Flat surface sediment water content of $\sim 29.3\%$ and a particle density of 2.5 g/cc. The diffusion coefficient D_2 was calculated from the relation $D_2 = \phi_2 D$ valid for low porosity sediment (Ullman and Aller, 1982) where D is the free solution diffusion coefficient for NH_4^+ at $T = 24^\circ\text{C}$ (Li and Gregory, 1974).

The measured value of ϕ_1/θ^2 for NH_4^+ in *Onuphis* burrow walls is ~ 0.36 , where θ is the tortuosity (Aller, 1983). Porosity of the tube wall including the agglutinated sand layer was found in the same study to be ~ 0.62 . For purposes of modeling the effect of changing burrow wall diffusion properties relative to adsorption effects, we assume the high porosity relationship $\phi_1 D_1 = (\phi_1/\theta^2)D \sim \phi_1^3 D$ when values of ϕ_1, D_1 at other than the measured values are necessary (Ullman and Aller, 1982). From the tube wall C content/tube wall volume relationships outlined in results (i.e. 7.37 mgC/cc tube wall), the porosity ϕ_1 (volume pore water/volume tube wall), and the adsorption isotherm of Figure 15, then $K_1 \sim 5.2$. This is calculated relative to volume pore water, that is: ($\mu\text{moles adsorbed NH}_4^+/\text{volume pore water}$)/($\mu\text{moles dissolved NH}_4^+/\text{volume pore water}$). Similar K_1 values for HPO_4^- and Si(OH)_4 are 9.3 and 4.3 respectively.

Using the above model values, the expected time variation of C_7 is shown in Figure 19 for the cases $K_1 = 0, K_1 = 5.2$, and $K_1 = 52$ with D_1 fixed; Figure 20 shows the additional cases of $\phi_1 D_1/32$ and $\phi_1 D_1/100$ with $K_1 = 0$ and Figure 21 illustrates the effect of varying the volume/surface area ratio of the reservoir: $h = 0.01, 0.1$, and 0.5 . The time dependence of burrow water concentration in Figure 19 ($K_1 = 5.2$) is similar to that actually observed (Fig. 5) indicating that the magnitudes of the model variables are reasonable. Relatively small changes in the adsorption coefficient, K_1 , influence the burrow water composition as much as large changes in either diffusive permeability of the tube lining ($\phi_1 D_1$) or variation in tube size. The effect of adsorption in particular is remarkable considering the fact that the tube lining is only 200 μm thick. Increasing the lining thickness at any given adsorption coefficient, K_1 , has the same relative effect

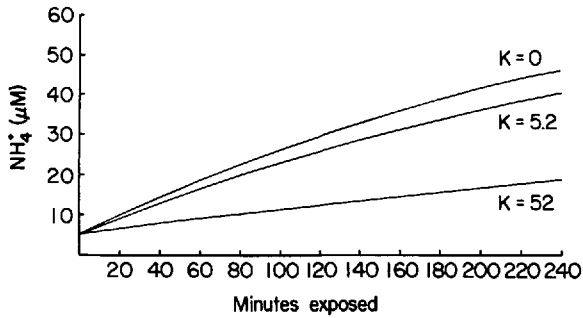


Figure 19. The predicted patterns of NH_4^+ concentration buildup in burrow water with burrow volume/wall area ratio $h = 0.1$ comparable to average *Onuphis* tubes. The effect of changing the adsorption coefficient, K , in the burrow lining on the transient concentration pattern is shown for the cases $K = 0, 5.2,$ and 52 .

as increasing K_1 at a fixed thickness. Changes in any one of the three variables can produce similar changes in time-dependent solute concentrations implying that differentiating the relative importance of, for example, adsorption and tube lining permeability on transient compositions of burrow water could not be done on the basis of time series concentrations alone.

In the case of a solute responding to zeroth order reactions, these effects of adsorption and permeability are restricted to the transient state behavior only; at steady state ($V, t \rightarrow \text{large}$) the solute flux across the tube wall is the same regardless of adsorption or diffusive characteristics (unless totally impermeable). On the other hand, the steady state as well as transient fluxes of a solute subject to first order or higher order kinetics can be greatly affected by tube lining properties (Aller, 1983).

These model calculations imply that simple adsorption is unlikely to be entirely responsible for the observed lack of concentration increase in a solute like HPO_4^- (Fig.

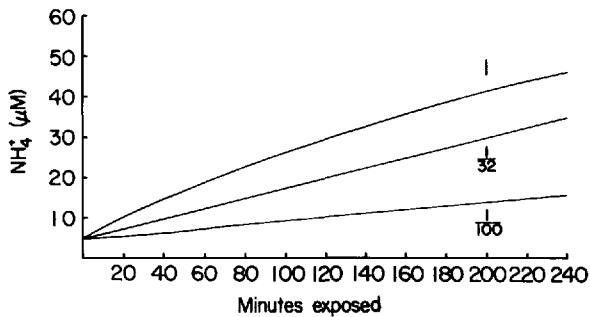


Figure 20. Predicted patterns of NH_4^+ concentration buildup in burrow water as in Figure 19 but in this case $K = 0$ in all cases and the factor, $\phi_1 D_1$, describing the diffusive permeability of the tube lining is varied by factors of $1/32$ and $1/100$ from the value given in the text.

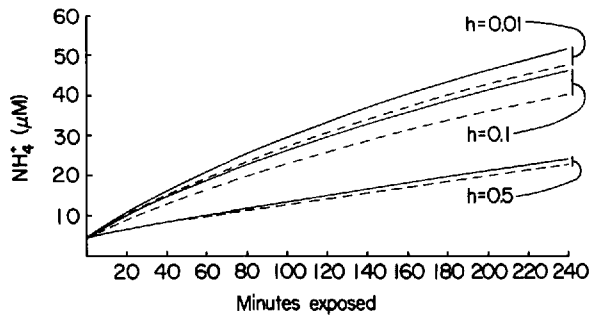


Figure 21. Predicted patterns of NH_4^+ concentration buildup in burrow waters for cases where burrow volume/wall area ratio varies from 0.01 to 0.5. The value of $\phi_1 D_1$ in the tube lining is the same as in Figure 19 in all cases. The solid line corresponds to an adsorption coefficient of $K = 0$ in the tube lining while the underlying dashed line corresponds to $K = 5.2$ in each case.

7). Although concentrations might be lowered by adsorption to 20–30% below the 2–3 μM expected, such a change should still be easily detectable above the 1 μM background. This is further evidence for a net precipitation reaction or perhaps uptake of HPO_4^- by bacteria in the burrow lining.

6. Conclusions

The composition of water contained in *Onuphis* and *Upogebia* burrows during ebb tide can be used as a sensitive indicator of biogenic and abiogenic reactions taking place within and around each burrow type. Transient excursions in burrow water composition are also sensitive to burrow geometry and adsorption-permeability properties of the inner lining or burrow wall. Both *Onuphis* and *Upogebia* burrow waters are influenced by a range of heterotrophic and chemoautotrophic microbial metabolic activity which occur in very close proximity. The balance between these and other reactions in each type of burrow differs, however, so that major differences in water composition can occur. *Upogebia* burrows show a greater net build-up than *Onuphis* of certain decomposition reaction products such as Mn^{++} , HPO_4^- , and ΣCO_2 and also apparently have much higher absolute rates of chemoautotrophic nitrification and associated denitrification. This latter conclusion is based on stoichiometric models and patterns of $\text{pH} - \Sigma\text{CO}_2$ differences between burrow types.

Other differences in burrow microenvironments are detectable despite spatial proximity of the two species. *Upogebia* burrows are undersaturated with respect to aragonite and calcite while those of *Onuphis* are supersaturated. Net precipitation or lack of net increase of HPO_4^- , $\text{Si}(\text{OH})_4$, and possibly Mn^{++} and Fe^{++} in *Onuphis* burrows implies the formation of authigenic mineral phases, probably nucleated by the organic tube lining. The standing number of bacteria are also higher in *Upogebia* than

Onuphis burrow water. This elevation in number may reflect the stimulation of bacterial growth related to the microbial gardening activity hypothesized for *Upogebia* (Frey and Howard, 1975; Ott *et al.*, 1976). It may also result from an inhibiting effect of enzymes in *Onuphis* tube linings (Zottoli and Carriker, 1974). In the absence of knowing feeding rates or other turnover factors in burrows during the intertidal, this difference can only be considered suggestive.

Rates of microbial metabolic activity as expressed in changes of burrow water composition appear to be somewhat higher in *Upogebia* than *Onuphis* burrow walls. As expected, these rates decrease during colder winter periods. The overall magnitudes of solute fluxes into both kinds of burrows are in the same range as net releases reported for fine-grained nearshore surface sediments during summer periods generally.

The organic tube lining of *Onuphis* has a high adsorption capacity for NH_4^+ , HPO_4^- , and $\text{Si}(\text{OH})_4$. Linear isotherms related to the amount of organic carbon present are found regardless of net charge of the solute in solution. This implies that the lining will act to concentrate a range of solutes and may act as a nucleation site for authigenic precipitates. Diffusion-reaction modeling demonstrates that even a very thin layer ($\sim 200 \mu\text{m}$) of this lining is capable of substantially influencing transient variations in burrow water composition, either through adsorption or permeability properties, although adsorption is relatively more important than permeability.

This study demonstrates the substantial biogeochemical heterogeneity that can be associated with particular burrow structures in the same general area. This variability may or may not be important in determining the average chemical properties of the sedimentary environment but will certainly be important in controlling the range of reactions possible. The exact way in which a burrow is constructed and maintained results in measurable changes in microbial community activity and the particular balances between abiogenic and biogenic reactions occurring within and around it. It seems likely that well-developed associations occur between certain kinds of microbes and the burrow structures of macroinfauna comparable to those reported for different groups of meiofauna (Aller and Yingst, 1978; Bell *et al.*, 1978; Thistle, 1979; Reise, 1981b). As emphasized in this and our previous studies, because burrows often closely correspond to boundaries between anoxic and oxic environments, these hypothesized associations must involve chemoautotrophs which catalyze reactions such as ammonia and sulfide oxidation. Perhaps geometric and functional analogues to terrestrial plant root-microbe relationships can be found in marine sediments.

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APPENDIX

The solution for the reservoir concentration, C_T , defined by Eqs. 8a, b, c and 9a, b, c, d, e, f is:

$$\begin{aligned}
 C_T = C_o &+ \frac{\phi_1 D_1 t}{h} \left(\frac{E_1}{\Delta_o} + \frac{E_2 L_1}{D'_1 \Delta_o} - 2a_2 L_2 \right) \\
 &- \frac{\phi_2 D_2 t}{h D'_2 \Delta_o} (L_1 - L_2)(R_1 + E_2) \\
 &+ \frac{\phi_1 D_1 E_2}{h \sqrt{D'_1}} \sum_{n=1}^{\infty} \frac{S_1 C_2 (\exp(-P_n^2 t) - 1)}{P_n^5 \Delta_n} \\
 &+ \frac{\phi_1 D_1 E_1}{h} \sum_{n=1}^{\infty} \frac{C_2 (\exp(-P_n^2 t) - 1)}{P_n^4 \Delta_n} \\
 &- \frac{\phi_2 D_2 R_1}{h \sqrt{D'_2}} \sum_{n=1}^{\infty} \frac{S_2 (\exp(-P_n^2 t) - 1)}{P_n^5 \Delta_n} \\
 &- \frac{\phi_2 D_2 E_2}{h \sqrt{D'_2}} \sum_{n=1}^{\infty} \frac{C_1 S_2 (\exp(-P_n^2 t) - 1)}{P_n^5 \Delta_n}
 \end{aligned}$$

Where:

$$D'_1 = D_1 / (1 + K_1)$$

$$D'_2 = D_2 / (1 + K_2)$$

$$E_1 = 2a_2(L_1 - L_2)((\phi_2 D_2 / \phi_1 D_1) - 1)$$

$$E_2 = 2a_2(\phi_1 D_1 L_2 + D'_1 h) / h$$

$$R_1 = R / (1 + K_2)$$

$$\Delta_o = 1 + (\phi_1 D_1 L_1 / h D'_1) - (\phi_2 D_2 (L_1 - L_2) / h D'_2)$$

$$S_1 = \sin(P_n L_1 / \sqrt{D'_1})$$

$$S_2 = \sin(P_n (L_1 - L_2) / \sqrt{D'_2})$$

$$C_1 = \cos(P_n L_1 / \sqrt{D'_1})$$

$$C_2 = \cos(P_n (L_1 - L_2) / \sqrt{D'_2})$$

$$\begin{aligned}
 \Delta_n = &((L_1 - L_2) - (\phi_2 D_2 L_1 / \phi_1 D_1) - (\phi_2 D_2 / P_n^2)) (C_1 S_2) / (2 \sqrt{D'_2} P_n) \\
 &+ (L_1 + (\phi_1 D_1 / h P_n^2) - ((\phi_2 (1 + K_2) (L_1 - L_2) D'_1) / \phi_1 D_1)) (S_1 C_2) / (2 \sqrt{D'_1} P_n) \\
 &+ (\phi_2 D_2 (L_1 - L_2) / D'_2 - \phi_1 D_1 L_1 / D'_1) (C_1 C_2) / (2 h P_n^2) \\
 &+ (\phi_1 D_1 (L_1 - L_2) - \phi_2 D_2 L_1) (S_1 S_2) / (2 h \sqrt{D'_1} \sqrt{D'_2} P_n^2).
 \end{aligned}$$

The values of P_n are the positive real roots of the equation:

$$C_2(C_1 + (\phi_1 D_1 S_1) / (h \sqrt{D'_1} P_n)) = -\phi_2 D_2 \sqrt{D'_1} S_2 (S_1 - (\phi_1 D_1 C_1) / (h \sqrt{D'_1} P_n)) / (\phi_1 D_1 \sqrt{D'_2}).$$

The number of roots required for accurate evaluation of C_T is dependent on the relative values of L_1 and L_2 when typical ranges of D_1 , D_2 , K_1 and K_2 are used. When $L_2 \gg L_1$ as is the case in this study, then the roots lie close to:

$$P_n = -n\pi \sqrt{D'_2} / (L_1 - L_2).$$

The roots may be readily found by use of an appropriately programmed hand calculator. Approximately 10 roots were used in the evaluation of the model curves of Figures 19, 20, and 21.

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