

Geochemistry of Burrow Waters Vented by a Bioturbating Shrimp in Bermudian Sediments *

D. G. Waslenchuk¹, E. A. Matson^{1,**}, R. N. Zajac¹, F. C. Dobbs¹ and J. M. Tramontano²

¹ Marine Sciences Institute, University of Connecticut; Groton, Connecticut 06340, USA

² College of Marine Studies, University of Delaware; Newark, Delaware 19711, USA

Abstract

Waters collected at various times from the burrows of *Callianassa* spp. shrimp are characterized chemically by concentrations of nutrients, sulfide and organic carbon, intermediate between those of pore waters and overlying waters of Coot Pond, Bermuda. Although the shrimp vigorously flush their burrows, irrigation events are insufficiently frequent to maintain a burrow water composition completely like that of oxygenated overlying waters; in instances where departure is extensive, models describing the diffusion of interstitial-water solutes into the water column via burrows would have to take this into account. Measured oxidation potentials are substantially reduced with respect to those of the water column, and relatively high levels of reduced arsenic (As III) are encountered. Burrow irrigation provides a mechanism for the rapid, conservative advection of solutes across the sediment-water interface and therefore is at least partially responsible for the concentration and speciation variations typical of coastal seawater. Of the solutes tested, only total dissolved inorganic arsenic occurs at seawater concentration in the burrows, implying that some specialized mechanism intercepts the diffusion of pore water arsenic into the burrows.

Introduction

We report here on a study in Bermudian inshore waters which characterizes the geochemistry of waters vented from burrows of the thalassinid shrimp *Callianassa* spp., relative to overlying and interstitial water chemistry in a shallow embayment. Consequently, the study provides a portion of the essential field data required for the verification of

physical-chemical models of the sediment-water interface. In one model of specific interest, Aller (1980) attempted to describe the burrow-irrigation phenomenon in terms of diffusion (biodiffusion), according to Berner's (1980) "general diagenetic equation". The model holds that pore-water solutes diffuse along a marked chemical gradient into the burrows of various tube-building infauna (burrowing shrimp, polychaetes, etc.), whereupon the solutes are delivered to the overlying water column as the resident organism flushes its burrow. Thus, for such bioturbated sediments, the flux of certain solutes across the sediment-water interface could be substantially increased over uni-directional gradient-driven fluxes of non-bioturbated sediments (Hartwig, 1974; Martens, 1976; Goldhaber *et al.*, 1977; Aller, 1978a, b; Aller and Yingst, 1978; Gust and Harrison, 1981) and pore water solute concentrations in general would be held to levels lower than those in non-bioturbated sediment (e.g. Klump and Martens, 1981).

The influence of burrow irrigation on early diagenesis and on the chemistry of the superjacent water-column will depend largely upon the vigor and frequency of irrigation, and upon the biogeochemical conditions maintained within and around the burrows. In the former case, the more often and thoroughly a burrow is flushed, the more the burrow water will resemble the oxygenated water column, and the steeper will be the chemical gradients between pore waters and burrow waters. Consequently, large fluxes of remineralized nutrients and minor elements, characteristically concentrated in pore waters, would be delivered to the water column. If flushing is not continuous, then burrow-water chemistry must vary repetitively, as pore-water solutes accumulate in "stagnant" burrows between flushes of superjacent seawater. In this case, gradients are not steady state, and biodiffusional rates will be lower.

The biogeochemical nature of the burrow environment also provides constraints to diagenesis and water-column chemistry. For example, tube- and burrow-dwelling infauna increase the area of the sediment-water interface,

* Contribution no. 907 from the Bermuda Biological Station

** Present address: Department of Biology, East Carolina University; Greenville, North Carolina 27834, USA

allowing products of microbial metabolism generated in adjacent anoxic sediment (Weiser *et al.*, 1974; Jørgensen, 1977a; Miller *et al.*, 1979; Barcelona, 1980) to diffuse across a larger area from anoxic to oxic conditions. However, this subsurface interface is not exposed to sunlight, so that the entire set of photoautotrophic processes (especially O_2 production and NH_4^+ and PO_4^{3-} uptake) is absent. In the absence of these photoautotrophic processes, burrowers and tube-builders must flush their habitat with oxygenated surface water to support their own metabolic requirements, and to satisfy the chemical and biochemical oxygen demands of diffused and "bioturbated" materials from adjacent sediments. Irrigation would therefore bring about a rapid and direct transfer of nutrients to seawater, bypassing possibly luxuriant microalgal mats covering the sediment surfaces. This rapid transfer mode might also allow soluble metal phases to avoid being trapped in the sediments by coprecipitation with insoluble metal oxides at the reduced-oxidized boundary near the sediment surface. It is conceivable though, that aphotic bacterial chemoautotrophic processes in part functionally replace the photoautotrophic ones (Kepkay and Novitsky, 1980). If solute removal mechanisms characteristic of the sediment-water interface are bypassed, then irrigation may produce greater net sediment to water fluxes than effected by other transfer regimes.

When the supply of oxidizable material to the burrow becomes greater than the supply of O_2 as a terminal electron acceptor (TEA) for aerobic respiration, anoxic metabolism would occur. A diverse set of reduced alternate TEAs would be generated, which then contain the energy transferred from the original organic material. These reduced species (e.g. NH_4^+ , NO_2^- , NO , N_2O , Fe^{+2} , S^{-2} , CH_4) and dissolved organic carbon from fermentations then become the basis for subsequent oxic metabolism (Wiebe, 1979), and for bacterial chemolithotrophic production (Jørgensen, 1977b) described as "benthic detrital electron flux" by Rich and Wetzel (1978). Here we report that gradients of reduced species do exist between pore and burrow waters in Bermudian sediments, bioturbated by the burrowing shrimp *Callianassa* spp.

Beyond exerting some controlling influence on chemical concentrations in interstitial waters, oxidation-reduction activity associated with bioturbators probably also influences the speciation of constituents. Reduced forms of solutes, such as Fe^{+2} and Mn^{+2} , would prevail if overall burrow-water chemistry is sufficiently reducing; alternately, biochemical electron transport can also directly cause indiscriminate reduction of minor species (such as Fe and Mn) during co-metabolism (Doelle, 1975) in addition to reduction of the major TEAs. The range of species which act as TEAs might be large, but we are limited in our knowledge because we can speciate so few elements. One of us (D. G. Waslenchuk) has experience with speciation of arsenic though, and we use the arsenic redox couple as an indication of the extent to which the biogeochemical nature of the burrow might affect speciation.

Material and Methods

Study Area

Coot Pond (area = 1.4 ha) is a shallow, 0.5 to 2 m, semi-enclosed basin on the island of St. George's, Bermuda. Tidal exchange occurs through a narrow, deep (3 m) channel connecting Coot Pond to North Lagoon, a coastal area bounded by a fringing reef. The pond is the surface expression of a collapsed cave, typical of karst regions. The bottom is composed of poorly sorted carbonate sediments. Two main biological features can be distinguished. Approximately 30 to 40% of the bottom is heavily bioturbated by *Callianassa* spp; another 40% is covered by *Thalassia* and other macrophytes; the remainder is open area among the macroflora. Mangroves border most of the pond's rocky perimeter.

Callianassa spp. was identified on the basis of fecal pellet and burrow morphology (Shinn, 1968; Aller and Dodge, 1974). There are two species of *Callianassa* reported from Bermuda (Biffar, 1971), *C. branneri* and *C. longiventeris*. For information on other species of *Callianassa* and burrowing shrimp in general, the reader is referred to Devine (1966; ecology), Aller and Dodge (1974; sediment reworking), Frey and Howard (1969) and Ott *et al.* (1976; tube morphology). Briefly, these medium-sized crustaceans (adults are ca 10 cm long) inhabit sandy sediments, constructing and living in burrows 1 m or deeper below the sediment surface. The shrimp cast up excavated sediment and fecal pellets, creating highly visible volcano-shaped mounds (50 cm height · 50–100 cm diameter) in Coot Pond. Propulsion comes from a current generated by synchronous beating of flap-like abdominal appendages (pleopods); the current also accomplishes water exchange between the burrow and overlying seawater. Casual observations indicate that "active" mounds are irrigated aperiodically, around the clock, and at all tidal stages. We assume that the effects on sediment geochemistry are independent of the exact species of *Callianassa*.

Field and Laboratory Procedures

The study was conducted in the period from August 16 to 27, 1980. Using ultra-cleaned plastic syringes (prepared for minor element studies), we sampled burrow waters from the exhalant plumes at the burrow openings, while a shrimp was actively irrigating, and also directly from the burrow interior, through a 10 cm length of Teflon tubing, during periods between pronounced flushing events of the burrow. A portion of each sample was carefully transferred to a vial for Eh measurements, another portion was put on ice for later NH_4^+ analyses, and the remainder was filtered in-line through a 0.2- μ m Nuclepore membrane; an aliquot of that was iced for up to two hours, then analyzed for PO_4^{3-} . The rest was quick frozen for later arsenic speciation and dissolved organic carbon (DOC) analyses. Separate syringe samples were obtained for sulfide analyses. In order to determine the chemical composition of overlying water, we took hourly water-column samples

over almost two tidal cycles (about 20 h) from two locations above the *Callianassa* spp. bioturbated area. These samples were taken by a snorkeler who submerged a closed one-liter polyethylene bottle to about 0.5 m depth, then opened the cap to allow the bottle to fill at arm's length. We assume that these samples represent compositions through the vertical, since the water column was shallow, turbulent due to waves and tidal currents, and was vertically isothermal and isohaline during the study period. Filtering and storage were as above. Reactive phosphate analyses were conducted according to Strickland and Parsons (1972), ammonium by the method of Solórzano (1969), DOC by thermal combustion according to Van Hall *et al.* (1965), arsenic speciation analyses by hydride-generation and plasma emission spectrophotometric detection (Waslenchuk, 1979) and sulfide was measured colorimetrically (Cline, 1969; Goldhaber, 1974). Eh was measured carefully by a well-cleaned electrode, taking care to avoid entraining air upon introduction of the electrode to a sample.

Results and Discussion

The analyses of 6 to 12 burrow-water samples and 32 water-column samples reveal the enrichment of several constituents in the burrows with respect to overlying seawater (Table 1). Burrow waters were enriched in phosphate, ammonia, and sulfide, both at times of active irrigation by a shrimp, and during intervening periods of quiescence. Concentrations of DOC and trivalent arsenic in burrow-waters were at least as high as maximum levels in overlying waters, and averaged much higher. Concentrations of methylated arsenic compounds were sought, but were everywhere below detection ($0.02 \mu\text{g As kg}^{-1}$). At no time did we obtain burrow water that had the overall low concentrations of overlying waters.

These results do show that the burrow water samples we obtained more closely resembled overlying waters than the Coot Pond pore waters examined by Lyons *et al.* (1979, 1980) (Table 1). Hence, Aller's (1980) assumption that burrow composition is equal to overlying water composition is fairly robust for this case. However, discontinuous flushing might allow burrow compositions to approach those of pore waters in other situations, and then it would be more appropriate to substitute an "expression" for the burrow-water composition (a variable upper boundary condition, $\partial C/\partial r$ being a function of time) instead of a constant (i.e. the steady state composition, where burrow water = seawater). To quantify that function will require a thorough description of burrow-water composition through time. More cogent, perhaps, would be a consideration of an alternative means by which to estimate the upwards flux of pore waters due to burrow irrigation. The flux could be treated as an advective transfer of burrow-water constituents, based on measurements of burrow compositions (as reported here) and measured irrigation rates. Such an approach would provide an independent estimate of flux, without requiring the very involved collection of pore waters.

Apparently, anoxic metabolism prevails within or adjacent to burrows, as sulfide is always measurable in burrow-water samples (Table 1). Measured Eh levels were negative in more than half our samples, even though some oxygenated Coot Pond water is intermixed with "pure" burrow water in samples from an exhalant plume of vented burrow-water. It is interesting to note that *Callianassa* spp. and other burrowing shrimp are commonly found in hypoxic marine sediments; their existence in an oxygen-poor, sulfide-rich environment is made possible by metabolic adaptations which include tolerance of anoxia (Thompson and Pritchard, 1969; Felder, 1979), reduced metabolism at low concentrations of oxygen (Torres *et al.*, 1977), a blood pigment (hemocyanin) with a high oxygen affinity (Miller and Van Holde, 1974), and burrow ventilation behavior related to oxygen concentration (Farley and Case, 1968).

Since the set of samples obtained from the burrows and their irrigation plumes represent various stages of mixing between "pure" burrow water and overlying water, it would be instructive to look for indications of the extent to which a solute is conserved during delivery to the water column by the irrigation process. This may be done by constructing a mixing diagram, where, for instance, observed ammonium concentrations are compared to those that would be predicted from a consideration of strictly non-reactive, physical mixing of two end-members (pure burrow water and overlying water). If mixing was ideal, in this sense, then a plot of ammonium concentration vs extent of mixing would be linear. In Fig. 1 such a linear relationship obtains, where the sample Eh is used as an indicator of the extent of mixing¹.

The relationship implies that both ammonium and the major redox-active ions which control Eh are conservatively exchanged between the dark, reduced burrow environment and the light, oxygenated water column. The Eh-setting major ion couples are oxygen/water, for air-saturated waters, and carbon and sulfur couples for anoxic waters (Turner *et al.*, 1981), hence oxygen, dissolved sulfur phases and dissolved carbon phases are evidently exchanged conservatively. Some support for the conservation of sulfur species comes from Fig. 2 where five data points,

¹ Eh is linearly proportional to the logarithm of the activity ratios of the major redox coupled species in solution:

$$\text{Eh} \propto \log \frac{\{\text{oxidized species}\}}{\{\text{reduced species}\}}$$

Since the speciations of the major Eh-setting elements are not controlled by equilibrium processes (i.e. by instantaneous reversible thermodynamics) over the short term, it is reasonable to assume that their activity ratios might vary ideally during mixing events lasting a few seconds. If so, Eh would be linearly related to extent of mixing, and could therefore be used as an indicator of mixing for mixing plots, such as Fig. 1. Given that these major ions have very different chemical reactivities than ammonium, and that they are linearly related (through Eh) to ammonium, all must be mixed conservatively. That the relationship should be linear for any other reason (than due to conservative mixing) would be fortuitousness in the extreme

Table 1. Composition of Coot Pond Waters^a

		Solute concentration in overlying water	Solute concentration in burrow water ^b	Solute concentration in pore water ^c
O-PO ₄	range	<0.02 – 0.40 μM l ⁻¹	1.5 – 2.5 μM l ⁻¹	6 – 12 μM l ⁻¹
	mean, no. of samples	\bar{x} = 0.17, <i>n</i> = 36	\bar{x} = 1.4, <i>n</i> = 10	
	std. deviation	σ = 0.10	σ = 0.8	
NH ₄ ⁺	range	0.6 – 11.6 μM l ⁻¹	15 – 64 μM l ⁻¹	300 – 900 μM l ⁻¹
	mean, no. of samples	\bar{x} = 4.5, <i>n</i> = 32	\bar{x} = 30, <i>n</i> = 12	
	std. deviation	σ = 2.8	σ = 16	
DOC	range	167 – 780 μM l ⁻¹	780 – 2 400 μM l ⁻¹	642 – 792 μM l ⁻¹
	mean, no. of samples	\bar{x} = 472, <i>n</i> = 3	\bar{x} = 1 478, <i>n</i> = 10	\bar{x} = 727, <i>n</i> = 6
	std. deviation	σ = 307	σ = 805	σ = 56
H ₂ S	range	<0.1 μM l ⁻¹	2.0 – 26 μM l ⁻¹	100 – 1 000 μM l ⁻¹ ^d
	mean, no. of samples		\bar{x} = 8.4, <i>n</i> = 6	
	std. deviation		σ = 8.9	
As ⁺⁵	range	1.23 – 1.63 μg l ⁻¹	1.08 – 1.75 μg l ⁻¹	
	mean, no. of samples	\bar{x} = 1.42, <i>n</i> = 10	\bar{x} = 1.48, <i>n</i> = 6	
	std. deviation	σ = 0.16	σ = 0.24	
As ⁺³	range	0.10 – 0.31 μg l ⁻¹	0.13 – 0.62 μg l ⁻¹	
	mean, no. of samples	\bar{x} = 0.20, <i>n</i> = 10	\bar{x} = 0.34, <i>n</i> = 6	
	std. deviation	σ = 0.07	σ = 0.19	
As ^{total dissolved}	range	1.33 – 2.48 μg l ⁻¹	1.38 – 2.29 μg l ⁻¹	13.8 – 35.6 μg l ⁻¹ ^f
	mean, no. of samples	\bar{x} = 1.71, <i>n</i> = 12	\bar{x} = 1.82, <i>n</i> = 6	\bar{x} = 22.5, <i>n</i> = 3
	std. deviation	σ = 0.30	σ = 0.30	σ = 11.6
$\frac{\{As^{+3}\}^g}{\{As^{+5}\}}$	range	0.26 – 0.87 μg l ⁻¹	0.30 – 1.61 μg l ⁻¹	
	mean, no. of samples	\bar{x} = 0.59, <i>n</i> = 10	\bar{x} = 1.0, <i>n</i> = 6	
	std. deviation	σ = 0.18	σ = 0.55	
Eh	range	+99 to +285 mV	–240 to +150 mV	
	mean, no. of samples	\bar{x} = 213, <i>n</i> = 18	\bar{x} = –16, <i>n</i> = 42	
	std. deviation	σ = 72	σ = 101	
pH		8.02 – 8.15	7.85 – 7.95	

^a All samples were filtered through 0.2-micron Nuclepore membranes, immediately after sampling and before preservation of the samples in the field. For burrow-water samples, an in-line membrane was attached to the syringe so that samples could be filtered into storage bottles without danger of oxidation (and subsequent precipitation) of dissolved constituents

^b Burrow waters were collected by drawing samples into 50-cc syringes, either from within the burrow through about 10 cm of Teflon tubing, or from the plumes of water that form above the burrow-mound while a shrimp actively flushes its burrow

^c Lyons *et al.* 1979 and 1980

^d Range of values reported by Lyons *et al.*, 1979, for 6 cores from Bermuda carbonate sediments, but not from Coot Pond. Presented here only for purposes of crude comparison

^f Subsamples of pore waters from cores collected in 1978, in Coot Pond, by Lyons *et al.*, 1980

^g Activity ratios were determined using an activity coefficient for the oxidized As V ion, H₂AsO₄⁻, of γ = 0.69, calculated by Davies' equation (Krauskopf, 1979), assuming that the ion is 100% free, and that As III occurs 100% as the uncharged H₃AsO₃ species

representing burrow and overlying water samples which could be analyzed for both Eh and ΣS^{2-} , suggest the requisite linear relationship. Furthermore, the linearity of the NH₄⁺ vs Eh plot illustrates well the "operational" usefulness of the platinum electrode. In waters of these intermediate Eh's, Pt⁰ is the stable phase of the metal, and the electrode is responsive to either the solution redox potential or a mixed potential (Whitfield, 1974), a conservative property in any case.

The high ammonium levels at negative Eh's are good evidence for the occurrence of extensive remineralization of nutrients (here, as ammonium) by anoxic metabolism in or adjacent to the burrows. Phosphate in the same burrow-

water samples does not behave similarly, perhaps because its concentration is controlled by reactions with solid mineral phases, such as by formation of insoluble Fe-Mn-PO₄ complexes (Klump and Martens, 1981), or by reaction with apatite grain coatings (Berner, 1980).

For anoxic waters whose redox level is controlled by the activities of carbon and sulfur species, the Eh should be about –270 mV (Turner *et al.*, 1981). If one assumes that the Eh of pure burrow water was similarly controlled, and extrapolates the curve in Fig. 1 to Eh = –270 mV, one can obtain an estimate of the ammonium concentration of that supposed end-member ... ca 110 μM l⁻¹. This level is 12–37% of the ammonium concentration of Coot Pond

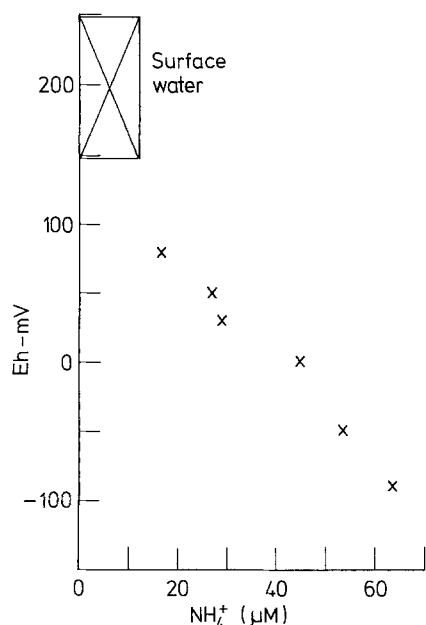


Fig. 1. *Callianassa* spp. Relationship between dissolved NH_4^+ concentration and measured oxidation potential (Eh) of *Callianassa* spp. burrow waters, sucked from within the burrows or from the plumes of vented water during irrigation events. Burrow water samples were collected from different burrows, during a one-hour period on August 19, 1980. Box at upper left shows range of overlying water values during the week of August 17, 1980

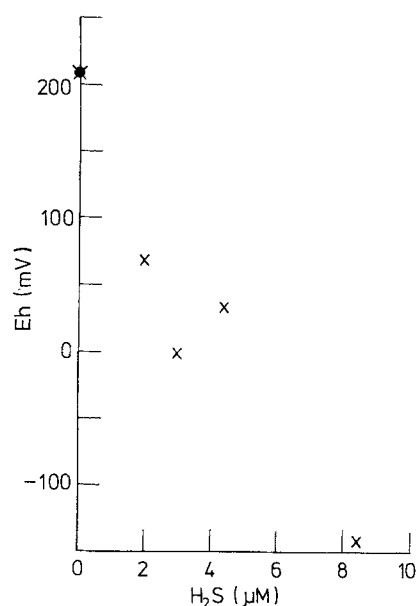


Fig. 2. *Callianassa* spp. Relationship between dissolved sulfide (as H_2S) and Eh for four samples from the exhalant plumes of individual *Callianassa* spp. burrows, and for average overlying waters

pore waters ($300\text{--}900\ \mu\text{M l}^{-1}$, reported by Lyons *et al.*, 1980), and perhaps reveals the closest approach of burrow composition to that of pore waters. It may be noted here that by estimating the end-member composition of the mixing series appearing in Fig. 1, a means to assess the extent of dilution of the samples is provided. One could calculate by the lever rule that the lower-most point in

Fig. 1 (64, -90) for instance, represents a sample made up by the proportions 42% overlying water: 58% pure burrow water. This calculation of the makeup of a sample, based on a conservative element, would allow one to predict the concentration of some other element, assuming it too was conservatively mixed. An observed concentration that was less than the predicted value would indicate the amount of removal the element must actually have undergone as it mixed unconservatively. In so doing, the reactivity of a constituent being transported by irrigation would be tested. Unfortunately, our phosphate data are insufficient, due to scatter, to allow us to project the phosphate concentration of the burrow water end member, therefore precluding the calculation of the predicted level. To increase the sophistication of this type of study, one evidently must collect a substantially larger number of samples of burrow waters.

Other evidence of the reduction of alternate terminal electron acceptors (other than O_2) by anoxic metabolism in or near the burrows might come from observations of arsenic speciation. In Table 1, high $\text{As}^{3+}/\text{As}^{5+}$ activity ratios reflect extensive reduction of arsenic in burrow waters, especially in those samples with low measured Eh values. The observed ratios would be at thermodynamic equilibrium in waters with oxidation potentials much lower (Eh of approximately -190 to -160 mV, by application of the Nernst-Peters relationship) than the measured Ehs for those samples. This disequilibrium implies that arsenic is either actively reduced in the burrow environment (i.e. is an alternate TEA), or that it has been reduced inorganically elsewhere in the sediments or deeper within the burrow where prevailing Eh is less than -160 mV. Sluggish oxidation kinetics (Sanders, 1979) might, in this case, prevent quick reestablishment of a new equilibrium at the Eh of the burrow waters sampled. Measurements of the arsenic species concentration ratio in overlying pond waters reveal values around 1:10, very similar to those values observed in coastal United States waters (Waslenchuk, 1979), which are also much out of equilibrium with the oxidation state of the water column. It should be noted that total dissolved arsenic concentrations are similar in burrow and pond waters. Irrigation is therefore not a transfer mechanism for total dissolved arsenic, but burrow waters are a source of reduced arsenic (As^{3+}) to the overlying water column. Irrigation of burrows is then probably partially responsible for the maintenance of arsenic species disequilibria in shallow coastal waters.

Of all constituents studied, only total dissolved inorganic arsenic concentrations were similar in burrow and overlying waters. Speculatively, one might invoke some exceptional chemoautotrophic transformation of pore water arsenic at the burrow wall which would intercept diffusing reduced arsenic. Certain arseno-lipids have been recognized in marine organisms, but cannot be detected by the arsenic speciation technique used here (Irgolic *et al.*, 1977; Wrench *et al.*, 1979). Thus, burrow irrigation may introduce an exotic phase of arsenic to the water column.

As an alternative to estimating the biodiffusive flux of interstitial water solutes across the sediment-water interface by a diffusion model such as Aller's (1980), it would be possible to estimate the flux as an "advected" contribution if irrigation rates were measured and coupled with observed burrow-water compositions. This remains to be done, but Gust and Harrison (1981) have recently pointed the way to doing so in a laboratory experiment where the irrigation flow rates of captured alpheid shrimps were measured with minute hot-wire anemometers. Application of the technique should be possible *in situ*, in protected shallow marine embayments. By following this approach, one might be able to assess fluxes due to irrigation without having to collect pore waters, a task made difficult by the necessity of preventing oxidation and other reaction artifacts during handling.

For a first look at the possible importance of irrigation to water-column composition though, a rough calculation can be made based on the data here, and on irrigation rates studied by Gust and Harrison (1981). The advective flux of a solute would be the product of its burrow water concentration and the irrigation rate of the community of *Callianassa* spp. For ammonium, the concentration range in burrows was 15–64 μM , the mean and standard deviation being $30 \mu\text{M} \pm 16$ (for 12 samples). Irrigation rate is estimated using data on the venting velocity of an alpheid shrimp (smaller than *Callianassa* spp., but builds burrows of the same diameter), measured in the laboratory by Gust and Harrison (1981). We chose 20 cm s^{-1} as a best estimate for *Callianassa* spp. irrigation velocity, since Gust and Harrison point out that at 20 cm s^{-1} the flow is laminar and more energy efficient than higher turbulent velocities. At 20 cm s^{-1} , burrow discharge would be ($20 \cdot$ cross-sectional area of a burrow opening at 0.7 cm diameter $= 20 \cdot 1.54 = 30.78 \text{ cm}^3 \text{ s}^{-1} = 1.85 \text{ l min}^{-1}$). At an irrigation frequency of four one-minute events per hour (the alpheid's rhythm), an individual *Callianassa* spp. will flush 7.4 l h^{-1} . The *Callianassa* spp. community would therefore transfer $7.4 \text{ l h}^{-1} \text{ individual}^{-1} \cdot 1 \text{ individual m}^{-2} \cdot 1.3 \cdot 10^3 \text{ m}^2$ of bioturbated bottom $= 9.6 \cdot 10^3 \text{ l h}^{-1}$.

The advection of burrow-water solutes into the water column should be manifested by cyclic concentration excursions in the water column. Since at high tide the Pond is most dilute ("new" water from offshore floods the Pond), concentrations should be minimal; over the next 6 h of the ebb, concentrations should build up due to burrow-water inputs. In six hours, the *Callianassa* spp. community would process $6 \cdot 9.6 \cdot 10^3 \text{ l}$ of Pond water, equivalent to 5% of the average volume of Coot Pond. Therefore, concentration in the water column should rise from a high tide minimum to a low tide maximum, the low tide maximum being estimated by:

$$\text{Max. } [\text{NH}_4^+] = 0.95 \cdot \text{high-tide } [\text{NH}_4^+] + 0.05 \cdot \text{burrow } [\text{NH}_4^+]$$

Our observations established average high-tide $[\text{NH}_4^+]$ at $2.0 \mu\text{M l}^{-1}$ and low-tide maximum $[\text{NH}_4^+]$ at $6\text{--}10 \mu\text{M l}^{-1}$, whereas this rough calculation would have ammonium

concentrations rising to $3.4\text{--}5.1 \mu\text{M l}^{-1}$, based on mean burrow concentrations and maximum burrow concentrations. In conclusion, then, it appears that *Callianassa* spp. irrigation alone might account for some 20–35% of the ammonium additions to the water column of Coot Pond.

Summary

First, irrigation of *Callianassa* spp. burrows is apparently not sufficiently frequent and vigorous to maintain burrow waters in a state chemically identical to overlying water. Rather, burrow waters are somewhat enriched in nutrients, sulfides and DOC. If enrichments were much greater than those observed here, one would need to adjust the concentration gradient boundary conditions for calculation of biodiffusive fluxes across the sediment-water interface.

Second, irrigation of burrow waters by *Callianassa* spp. provides a mechanism for injecting pore water constituents into the water column, and at least for ammonium, allows the nutrient consuming photoautotrophic community residing at the lighted sediment-water interface to be bypassed. Since burrow waters do not have the exact composition of overlying seawater, it may be possible to estimate upwards solute fluxes due to irrigation by measuring burrow concentrations and irrigation rates, hence providing an alternative to biodiffusion models.

Third, the ubiquitous presence of sulfides, and the low Eh levels measured in burrow waters, suggest that anoxic metabolism prevails amongst an associated microbial community adjacent to or within the burrows, and provide further indications of the capacity for stress-tolerance exhibited by burrowing shrimp.

Fourth, arsenic evidently becomes an electron acceptor in burrow or pore waters, where a complex set of metabolic oxidation-reduction reactions must occur based on largely anoxic catabolism of organic matter. The burrows are sources of reduced arsenic (As^{+3}) to the water column, and burrow irrigation may thus be partially responsible for the maintenance of observed arsenic species disequilibria in coastal waters.

Acknowledgements. This study was supported in part by an Exxon Fellowship (administered through the Bermuda Biological Station) to D. G. Waslenchuk. We thank W. Berry Lyons for supplying us with subsamples of his pore waters from Bermuda, and thank the BBS staff for their cooperation. We are grateful to two anonymous reviewers for their insightful comments, which helped us to present this paper more clearly.

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