JOURNAL OF MARINE RESEARCH

The *Journal of Marine Research,* one of the oldest journals in American marine science, published important peer-reviewed original research on a broad array of topics in physical, biological, and chemical oceanography vital to the academic oceanographic community in the long and rich tradition of the Sears Foundation for Marine Research at Yale University.

An archive of all issues from 1937 to 2021 (Volume 1–79) are available through EliScholar, a digital platform for scholarly publishing provided by Yale University Library at https://elischolar.library.yale.edu/.

Requests for permission to clear rights for use of this content should be directed to the authors, their estates, or other representatives. The *Journal of Marine Research* has no contact information beyond the affiliations listed in the published articles. We ask that you provide attribution to the *Journal of Marine Research.*

Yale University provides access to these materials for educational and research purposes only. Copyright or other proprietary rights to content contained in this document may be held by individuals or entities other than, or in addition to, Yale University. You are solely responsible for determining the ownership of the copyright, and for obtaining permission for your intended use. Yale University makes no warranty that your distribution, reproduction, or other use of these materials will not infringe the rights of third parties.

The measurement of sediment irrigation rates: A comparison of the BR⁻ tracer and ²²²RN/²²⁶RA disequilibrium techniques

by W. R. Martin[1] and G. T. Banta[2,3]

ABSTRACT

We have carried out a series of experiments designed to allow comparison of sediment irrigation rates determined simultaneously using two methods: the measurement of ²²²Rn/²²⁶Ra disequilibrium in pore waters, and the measurement of distributions of a tracer, Br⁻, which was added to the water overlying sediments at the start of incubation experiments. The experiments were carried out on fine-grained sediments from Buzzards Bay, MA. We made irrigation rate measurements on sediments in their natural state, as well as on sediments that had been treated to alter macrofaunal abundance and diversity. The range of irrigation rates measured was similar for both tracers, and was similar to rates measured at the study site previously by Martin and Sayles (1987). Furthermore, the two tracers gave similar patterns of irrigation rate variability between cores and with depth below the sediment-water interface. On the other hand, comparisons of individual cores showed significant differences in the absolute rates measured using the different tracers; in particular, the ²²²Rn/²²⁶Ra disequilibrium method yielded more rapid irrigation rate estimates at depths exceeding 10 cm below the sediment-water interface. These differences could be due to the inherent limitations on the sensitivity of the methods, to artifacts in measurement procedures, to differences in the permeability of burrow walls to the two tracers (Rn and Br⁻), or to differences in the time-scales on which the two tracers record irrigation events. Irrigation rates determined by the Br⁻ tracer method were roughly correlated with the abundance of *Nephtys incisa* in the sediments, but were not related to abundances of the other numerically important deposit feeders, *Nucula annulata* and *Mediomastus ambiseta*.

1. Introduction

The burrowing and feeding activities of sediment infauna play an important role in the early diagenesis of continental margin sediments. By facilitating the exchange of solutes between pore waters well below the sediment-water interface and overlying seawater, they influence distributions of dissolved reactants and products of early

1. Department of Chemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543, U.S.A.
2. Boston University Marine Program, The Ecosystems Center, Marine Biological Laboratory, Woods Hole, Massachusetts, 02543, U.S.A.
3. Present address: Institute of Biology, Odense University, Campusvej 55, DK-5230 Odense M, Denmark.

diagenetic reactions (e.g., Aller, 1980a,b; Christensen *et al.,* 1984; Aller and Yingst, 1985; Archer and Devol, 1991) as well as sediment composition. In particular, sediment irrigation influences the preservation rates of both organic carbon (Christensen *et al.,* 1984; Archer and Devol, 1990) and $CaCO_3$ (Aller, 1982). The measurement of irrigation rates is essential to the use of profiles of pore water solutes to determine reaction rates and fluxes across the sediment-water interface.

Several methods have been used to determine sediment irrigation rates. The combination of closed system sediment incubations, which permit the determination of reaction rates independently of transport processes, with pore water profiles allows the determination of irrigation rates directly from profiles of the affected solutes (Aller, 1980a,b; Christensen *et al.,* 1984). Alternatively, irrigation rates have been estimated from fluxes and pore water profiles of tracers that are believed to be unreactive or tracers with known reaction rates. The latter experiments have been carried out using both steady-state distributions of a naturally occurring tracer with a known reaction rate ($^{222}Rn/^{226}Ra$ disequilibrium: e.g., Key *et al.,* 1979; Smethie *et al.,* 1981; Christensen *et al.,* 1984; Hammond *et al.,* 1985; Martin and Sayles, 1987), and transient-state distributions of radioisotopic tracers (e.g., tritiated water: Emerson *et al.,* 1984; ^{22}Na: Luedtke and Bender, 1979). A different approach is to use the difference between fluxes of particular solutes measured directly, via benthic flux chambers, and diffusive fluxes derived from pore water profiles to estimate irrigation rates (Berelson *et al.,* 1987; Archer and Devol, 1990). While all of these methods have been useful in establishing the importance of sediment irrigation to early diagenesis, each method has limitations. The closed system incubation/pore water profile method is only useful in shallow waters, as the isolation of sediment sections under *in situ* conditions is impossible in deep water. The comparison of directly measured fluxes to diffusive fluxes requires knowledge about the rates of reactions occurring too close to the sediment-water interface to be resolved by pore water profiles. Methods using tracers require knowledge about the relationships between irrigation rates of different solutes; because the permeability of burrow walls may vary between different solutes, this information is difficult to obtain (Aller, 1983). It appears that the most reliable way to determine irrigation rates is to use a variety of methods.

Monitoring irrigation rates during benthic flux experiments poses special problems. Tracer techniques are advantageous because they allow the use of independently determined irrigation rates to determine the relative importance of diagenetic reactions at the interface and within the sediment column. The naturally-occurring irrigation tracer, $^{222}Rn/^{226}Ra$ disequilibrium in pore waters, yields a signal that is integrated over a two to three week period (Smethie *et al.,* 1981), longer than most incubation experiments. In addition, measurement of the Rn flux requires large samples, and determination of even the vertically-integrated irrigation rate requires additional information on the production rate of ^{222}Rn in pore waters. Radiotracers

introduced into the overlying water at the start of incubations require extensive handling precautions, making their use extremely labor-intensive.

An alternative, artificially introduced tracer is Br^-. The Br^-/Cl^- ratio in seawater is constant, indicating quasi-conservative behavior (Morris and Riley, 1966). Br undergoes no redox cycling in seawater. Although it is released during the early diagenesis of organic matter (Price and Calvert, 1977; Pedersen and Price, 1980; Mayer *et al.,* 1981; Fischer *et al.,* 1986), the rate of release is not rapid enough to change the Br^- concentration in pore waters significantly. Thus, it is potentially well-suited for use as a transport rate tracer. We have conducted a series of tests using nearshore sediments from Buzzards Bay, MA, to determine the suitability of Br^- as an irrigation rate tracer during sediment incubations. We have made measurements to verify that natural Br^- cycling does not affect its concentration in the pore waters of the sediments we used for our tests, and to show that the addition of NaBr to the sediments does not measurably alter sediment respiration or irrigation rates; and we have compared sediment irrigation parameters determined using the Br^- tracer method to those determined on the same sediment cores using the $^{222}Rn/^{226}Ra$ disequilibrium method.

2. Methods

a. Sampling site. We determined irrigation rates in sediments collected from a site near the Weepecket Islands in Buzzards Bay, MA. Water column depth at the sampling site is 15 m. The sediments at the site are about 17% clay, 93% silt/clay (Moore, 1963). The macrofaunal community is dominated by deposit feeders, which make up 70–90% of the macrofauna present (Sanders, 1958). The dominant species are the small polychaete, *Mediomastus ambiseta,* the bivalve, *Nucula annulata,* and the errant polychaete, *Nephtys incisa* (Sanders, 1958; Sanders, 1960; Grassle and Grassle, 1984; Whitlatch *et al.,* unpubl. ms.). The sediments are rapidly mixed in the upper 3 cm of the sediment column (Martin and Sayles, 1987), and bioturbation, as recorded by ^{210}Pb and ^{14}C profiles, is significant to depths of 30 cm or more (Farrington *et al.,* 1977; McNichol *et al.,* 1988; Brownawell, 1986). Pore water irrigation is important during the warm months in at least the upper 20 cm of the sediment column (Martin and Sayles, 1987). Benthic respiration at the site is rapid and seasonally variable. The average rate of organic carbon degradation is about 600 $\mu mol\ C/cm^2/yr$ (McNichol *et al.,* 1988).

b. Sediment handling and sampling. The sediments analyzed during this study were collected by SCUBA divers in May, 1988 and in September, 1989. All the 1988 cores and all but one of the 1989 cores were 15 cm in diameter; the remaining one was a 6.5 cm diameter core that was collected for measurement of $^{222}Rn/^{226}Ra$ disequilibrium only. The 7 cores collected in May, 1988 were maintained in a seawater bath at *in situ* temperatures until August, 1988. For most of that period, the core tops were

Table 1. Sediment sampling and manipulation.

A. Sampling and treatment dates

Core	Collection	Manipulation	Incubation	Irrig. Meas.*	
				Rn	Br
N1	25 May, '88	June, '88	16–18 Aug., '88	x	x
D1	25 May, '88	June, '88	22–24 Aug., '88	x	x
M1	25 May, '88	June, '88	14–16 Aug., '88	x	x
U1	25 May, '88	None	28–30 Aug., '88	x	x
D2	25 May, '88	June, '88	24–26 Aug., '88	—	x
N2	25 May, '88	June, '88	24–26 Aug., '88	—	x
U2	Aug., '88	None	30 Aug.–1 Sep., '88	—	x
RF1	11 Sept., '89	None	None	x	—
BF1	11 Sept., '89	None	None	—	—
BF2	11 Sept., '89	None	None	—	—
L1	11 Sept., '89	None	13–15 Sept., '89	x	x
L2	11 Sept., '89	None	11–13 Sept., '89	x	x

B. Treatments: 1988 cores

Core	Defaunated	None	Polychaete addition	
			Mediomastus	*Nephtys*
N1	Yes			x
D1	Yes	x		
M1	Yes		x	
U1	No	x		
D2	Yes	x		
N2	Yes			x
U2	No	x		

Notes: *These columns show (with an x) the methods used to determine irrigation rates for each core.

open, and pore water solutes could exchange freely with overlying water. Periodically, the core tops were sealed to monitor sediment oxygen demand. In contrast, the 1989 cores were sealed for benthic flux measurements at the *in situ* temperature only once, one (core L2) or two (core L1) days after their return to the laboratory.

The 1988 cores were subjected to a variety of treatments (Table 1). Five of the seven cores were manipulated in June, 1988 in order to change macrofaunal composition. First, the cores were sealed and the O_2 concentration in the overlying water was allowed to drop to low levels. This procedure tends to drive infauna to the sediment surface (Bishop, 1952). Then, the upper 2–3 cm of the sediments were removed and sieved through 300 μm screens. The remainder of the sediment core was allowed to become completely anoxic and was left in that state for 17 days. This combination of steps removed or killed most of the organisms originally present in the sediments. Following the defaunation procedure, the sieved surficial sediments were added back to the cores. Then, O_2 was allowed to re-enter the system, and

Nephtys or *Mediomastus* were added to some cores (Table 1). After being maintained in the seawater bath for two months, the manipulated cores were sealed, with overlying water in place; NaBr was added in order to raise the Br⁻ concentration in the overlying water to about 10 mM (compared to the ambient concentration of about 0.8 mM); and the overlying water was stirred during a 1.5 day incubation.

The 15 cm diameter cores were subcored immediately after the final incubations. Three 6.5 cm i.d. subcores were taken from each. One was sectioned at 1 cm intervals; pore waters were separated from the sediments by centrifuging and were used for the determination of Cl⁻ and Br⁻ concentrations. A second 6.5 cm i.d. subcore was sectioned, and the sediment sections were sealed in gas washing bottles for determination of the pore water ^{222}Rn activity and the secular equilibrium value of the ^{222}Rn activity (Key *et al.,* 1979). The top 10 cm of the remaining 6.5 cm i.d. subcore was sieved through a 300 μm screen; the material retained on the screen was preserved in 10% buffered formalin for later characterization of the macrofauna present. Two smaller subcores (2.5 cm i.d.) were taken. These were used to determine Br⁻ and Cl⁻ concentrations at 3 mm intervals in the upper 3 cm of the sediments and to determine sediment porosity.

c. Analytical methods. We measured Br⁻ and Cl⁻ concentrations by ion chromatography (Dionex 2010i Ion Chromatograph with AS-3 anion column and anion micromembrane suppressor) after diluting samples 500-fold with distilled, deionized water. We normalized Br⁻ concentrations to a constant Cl⁻ concentration, which we determined separately for the 1988 and 1989 cores by averaging all the Cl⁻ measurements from each set. We subtracted the *in situ* Br⁻ concentration from our measured values to determine excess Br⁻. The *in situ* concentration was determined from pore waters taken from unspiked cores in 1989; we used the Br⁻:Cl⁻ ratio obtained from these measurements and pore water Cl⁻ measurements to infer the *in situ* Br⁻ concentration for the 1988 cores. The relative uncertainty in excess Br⁻ determinations ranged from ±2.5% in surficial sediment samples to ±0.02 mM in deep samples with small excess Br⁻ concentrations.

We measured pore water Rn concentrations within 36 hours of sample collection. Rn was extracted from the samples by circulating He through them, at 1 atm. pressure, for 45 minutes (Mathieu, 1988). After leaving the sample, the carrier gas passed through Drierite and Ascarite to remove H_2O and CO_2, and Rn was collected in a stainless steep trap at liquid nitrogen temperature (Key *et al.,* 1979). The extracted gas was then transferred to counting cells for ^{222}Rn scintillation counting on an Applied Techniques model DRC-MK6 Dual Radon Counter. The sediment samples were transferred to glass bottles for storage. Later, they were returned to gas washing bottles, the Rn was removed by purging with He for 45 minutes, and the bottles were sealed. After 1–2 weeks for Rn ingrowth, pore water Rn was extracted from the sample as outlined above. This measurement gave the value of the ^{222}Rn

activity that would occur in a closed system, in secular equilibrium with ^{226}Ra (which we will call Rn_{eq}). The uncertainties in pore water ^{222}Rn measurements are 5–15% of the measured values, while Rn_{eq} values are known to $\pm 3.5\%$. The resulting uncertainties in pore water Rn deficits (Rn_{eq} minus the pore water ^{222}Rn activity) are shown in Figure 4.

Macrofauna were characterized after sieving sediments with a 300 μm screen and preserving samples in 10% buffered formalin. Samples were stained with Rose Bengal to aid in sorting animals from detrital material. Benthic animals were identified using a dissecting microscope to at least family level; the more important members of the community were identified to species level.

3. A model of sediment-seawater exchange due to sediment irrigation

a. Basic assumptions about irrigation. Biologically driven sediment irrigation occurs when the burrows of sediment infauna, which are filled with overlying seawater that can exchange solutes with pore waters, are flushed frequently due to the animals' activities. The process is important to the exchange of solutes between sediment pore waters and overlying seawater because it allows exchange between seawater and pore waters that are well below the sediment-water interface. The two steps driving this exchange are diffusive transport of solutes across burrow walls and rapid exchange of burrow waters with overlying seawater (Aller, 1980a,b). The process can be described by a nonlocal exchange parameter, α (dimensions: 1/time), such that the rate of change over time of the concentration of a pore water solute due to irrigation is given by (Christensen *et al.*, 1984; Emerson *et al.*, 1984; Boudreau, 1984):

$$\left(\frac{\partial \phi C}{\partial t}\right)_{irr} = \alpha \phi (C_{olw} - C) \tag{1}$$

at each depth below the sediment-water interface. C is the solute concentration in pore waters and C_{olw} is its concentration in the overlying water; ϕ is porosity. In this formulation, the factors that determine the value of α are:

(1) The density (number per area of sediment), size, and shape of burrows, all of which determine the surface area available for solute exchange (Aller, 1980);

(2) The burrow properties that affect the rate of diffusion of solutes across burrow walls: their thickness, porosity, and reactivity with solutes (Aller, 1983);

(3) The diffusivities of individual solutes;

(4) Deviations from the model affecting the inferred value of α. In particular, if burrows are sporadically or imperfectly flushed, solute concentrations in burrow waters will differ from their concentrations in overlying water (Aller *et al.*, 1983). Since we cannot measure concentrations in burrow waters, these deviations from the model assumptions will be seen as variations in the value of α (Hammond *et al.*, 1985).

All of these factors may vary with depth below the sediment-water interface. We

assume that α varies exponentially with depth in the upper 20 cm of the sediment column:

$$\alpha = \alpha_0 e^{-\alpha_1 x}. \tag{2}$$

The Br$^-$ profile for one core, L2, could not be fit adequately with this simple form for the depth-variation of α. In this case, we specified a constant α (whose value was determined by least-squares fit to the data) in the upper 1 cm of the sediments, and allowed α to decrease smoothly with depth below the upper 1 cm.

b. Application of the irrigation model to Br$^-$ tracer profiles. Br$^-$ can be used as a tracer of sediment-seawater exchange in the following way. A known volume of water is enclosed over a sediment column. The overlying water is well mixed. A few minutes after sealing the sediments and overlying water, NaBr is added to the overlying water in an amount that is sufficient to raise its Br$^-$ concentration to about ten times the *in situ* level. During the course of the incubation, Br$^-$ is transferred to pore waters by diffusion across the sediment-water interface and by nonlocal exchange driven by the activities of the infauna.

If the volume of the water overlying the sediments is sufficiently great, the concentration of Br$^-$ in it will remain unchanged throughout the experiment. In this case, since the Br$^-$ distribution is not affected by adsorption to sediments (Aller, 1983), the distribution of Br$^-$ in pore waters at time t is described by:

$$\frac{\partial(\phi C)}{\partial t} = \phi \frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(\phi D_s \frac{\partial C}{\partial x}\right) - \alpha\phi(C - C_{olw}) \tag{3}$$

with boundary conditions,

$$C(x = 0, t > 0) = C_{olw} \tag{3a}$$

$$\frac{\partial C}{\partial x}(x = x_{max}, t > 0) = 0 \tag{3b}$$

$$C(x, t = 0) = C_0 \tag{3c}$$

(ϕ is the porosity of the sediments, D_s is the diffusion coefficient for Br$^-$ in the sediments, x_{max} is the depth of the bottom of the incubated sediment column, and C_0 is the initial distribution of excess Br$^-$ in the pore waters). Porosity is constant over time, but is allowed to vary exponentially with depth (with the parameters in $\phi = a + be^{-cx}$ determined by least squares fits to measured ϕ profiles), and $D_s = D_{sw}\phi^2$. At the beginning of the experiment, $C_0 = 0$, and C_{olw} is the concentration of excess Br$^-$ in the overlying water column resulting from the addition of NaBr.

To describe the progress of the experiments accurately, C_{olw} must be allowed to vary with time. Thus, Eq. (3) is solved for a very short time period ($t = \delta t$), and the change in C_{olw} due to Br$^-$ transferred to the pore waters during that period is

determined by

$$C_{olw}(t + \delta t) = C_{olw}(t = 0) - \frac{\int_0^{x_{max}} \phi C(x, t)dx}{h} \tag{4}$$

where h is the height of the column of water overlying the sediments. Then, C_0 is reset to the current Br⁻ distribution, and the distribution at the end of the next time step is found using Eq. (3) and the new C_{olw}. We have solved the differential equation numerically using the Crank-Nicolson procedure (Crank, 1975), checking the accuracy of this approach by comparing solutions for a simple case, with no irrigation and constant ϕ and D_s, to the analytical solution for that case (Bender *et al.,* 1987). The two solutions agreed to within a few parts in 10^5 for the values of δt and δx (the grid spacing in the depth coordinate) that we chose for our routine model runs.

For this study, whose primary focus was on sedimentary metabolism (Banta, 1991), we used short incubations (1–1.5 days long) in order to avoid depletion of dissolved O_2 in overlying waters to values below 70 μmol/l. In general, longer incubations can be carried out by aerating the water overlying the sediments. The short duration of the incubations has important implications for the interpretation of excess Br⁻ profiles (Fig. 1). The sensitivity of Br⁻ profiles to variations in irrigation rate parameters (in particular, to α_0 and α_1 in Eq. (2)) increases steadily as incubation time increases up to an optimum time beyond which the homogenizing effects of mixing processes become important. This upper limit in useful incubation time is determined by irrigation rates, by the height of the column of water overlying the incubated core, and by the thickness of the sediment layer incubated. For short incubations, vertically oriented molecular diffusion is the primary mechanism of tracer transport near the sediment-water interface because of the large concentration gradient there. Thus, rapid irrigation is needed to produce measurable differences in excess Br⁻ concentration profiles close to the interface, and the profiles are most sensitive to variations in irrigation rates at depths of 3–5 cm, near the deepest point to which Br⁻ can penetrate by vertical molecular diffusion (Fig. 1).

c. Application of the irrigation model to $^{222}Rn/^{226}Ra$ *disequilibrium profiles.* There are two differences between the measurement of irrigation rates by the Br⁻ tracer and Rn disequilibrium techniques. First, the source of Br⁻ to the pore waters is the spike added to overlying water. In contrast, the source of ^{222}Rn is its production within the sediments due to the decay of ^{226}Ra. Thus, sediment-seawater exchange of solutes produces an excess of Br⁻ in the sediment pore waters and a deficit of ^{222}Rn relative to the amount that would be present in the absence of sediment-seawater exchange. Second, while the excess Br⁻ profile is by its nature a transient-state phenomenon and is determined by processes occurring only over the length of the incubation experiment, the Rn disequilibrium profile averages the effects of processes occurring
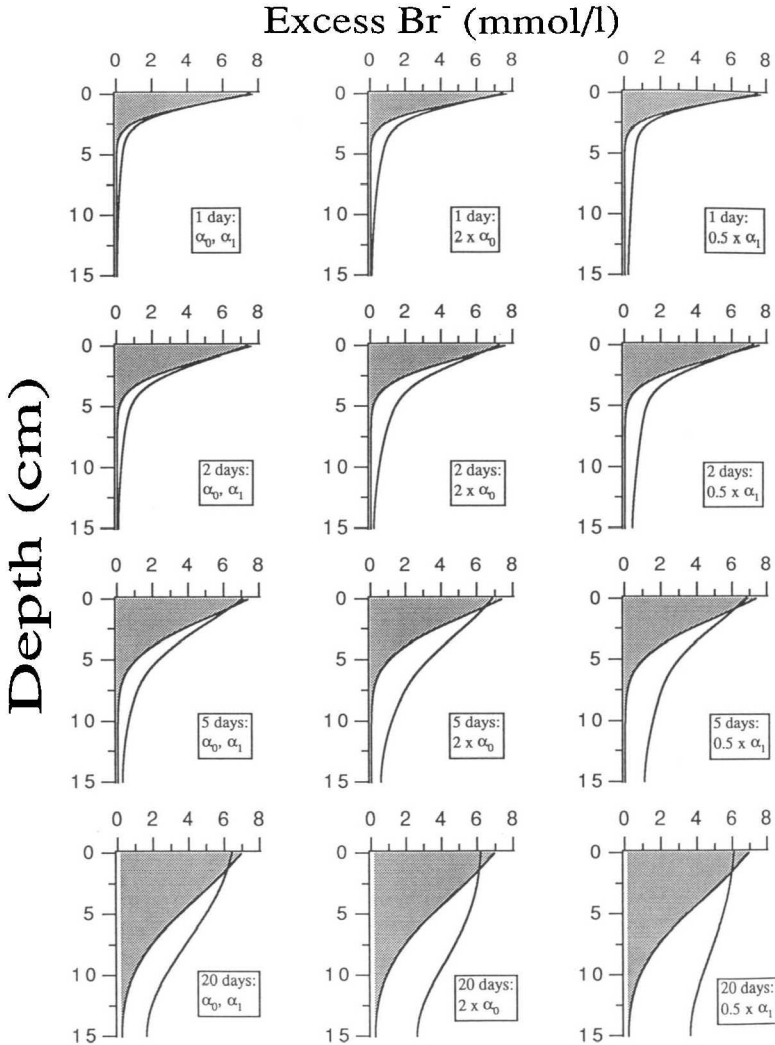
Excess Br⁻ (mmol/l)

Figure 1. The sensitivity of excess Br⁻ profiles to variations in the irrigation rate parameters, α_0 and α_1. Sensitivity to variations is shown for 4 incubation lengths: 1 day, 2 days, 5 days, and 20 days. In each graph, the shaded area indicates the profile that would be produced by molecular diffusion alone for the incubation conditions, and the solid line indicates the profile resulting from diffusion plus irrigation at the rate specified by the α_0 and α_1 values used. The baseline α_0 and α_1 values were the best-fit values for core U1 (Table 4).

over a two to three week period, with more recent events weighted more heavily in the averaging process (the half-life of ^{222}Rn is 3.82 days, compared to 1600 years for its parent, ^{226}Ra) (Smethie *et al.*, 1981).

The irrigation model, applied to ^{222}Rn/^{226}Ra disequilibrium, reflects these differences from the Br⁻ case. The Rn disequilibrium profile is assumed to be in steady

state. The ^{222}Rn activity in the overlying water before cores were sealed for flux measurements was below our detection limit. The activity at the end of the incubations was still less than 5% of the equilibrium ^{222}Rn activity in the surficial sediments. Thus, the change in ^{222}Rn profiles during the course of the incubations was small, and the steady state assumption is a reasonable approximation. We also assume that plugging the bottoms of cores that were incubated immediately after collection (cores L1 and L2) did not affect the Rn profiles. Thus, we applied an "open system" bottom boundary condition to these cores (Eq. 5b below). This condition allows a nonzero gradient at the bottom of the pore water Rn profile. We used a transient-state model to confirm that sealing the bottoms of cores did not affect the Rn distribution significantly over the time period of the incubations. For the remainder of the cores, all of which were kept for several weeks with sealed bottoms, we adopted a "closed system" bottom boundary condition (Eq. 5c). With these assumptions, the pore water Rn profile is described by (Christensen *et al.*, 1984; Emerson *et al.*, 1984; Hammond *et al.*, 1985; Martin and Sayles, 1987):

$$\frac{d}{dx}\left(\phi D_s \frac{dC}{dx}\right) - \phi(\lambda + \alpha)C + \lambda\phi P(x) = 0. \tag{5}$$

At the sediment-water interface,

$$C(x = 0) = 0. \tag{5a}$$

At the base of the incubated sediment column, the open-system condition:

$$C(x = x_{max}) = \frac{\lambda P(x_{max})}{\lambda + \alpha(x_{max})}. \tag{5b}$$

The closed-system condition:

$$\frac{dC}{dx}(x = x_{max}) = 0. \tag{5c}$$

C is the ^{222}Rn activity (dpm/cm$^3_{pw}$). D_s is the sedimentary diffusion coefficient for Rn. α, ϕ, and D_s vary with depth in the same ways as in the Br$^-$ model. λ is the radioactive decay constant for ^{222}Rn. $\lambda P(x)$ is the pore water ^{222}Rn activity at secular equilibrium with ^{226}Ra (Key *et al.*, 1979). Eq. 5b is the open-system bottom boundary condition, and Eq. 5c is the closed-system bottom boundary condition, allowing no exchange across the plug at the bottom of the core. We solved the differential equation numerically, with a relaxation technique (Press *et al.*, 1986), using cubic spline representations of our measured $P(x)$ profiles.

Pore water ^{222}Rn profiles and Rn$_{eq}$ from the cores taken in September, 1989 can be used to examine the sensitivity of Rn profiles to variations in the irrigation rate parameter. These 3 cores (cores RF1, L1, and L2) had very similar Rn profiles, which we have averaged to produce the data shown in Figure 2. The ranges in Rn activities
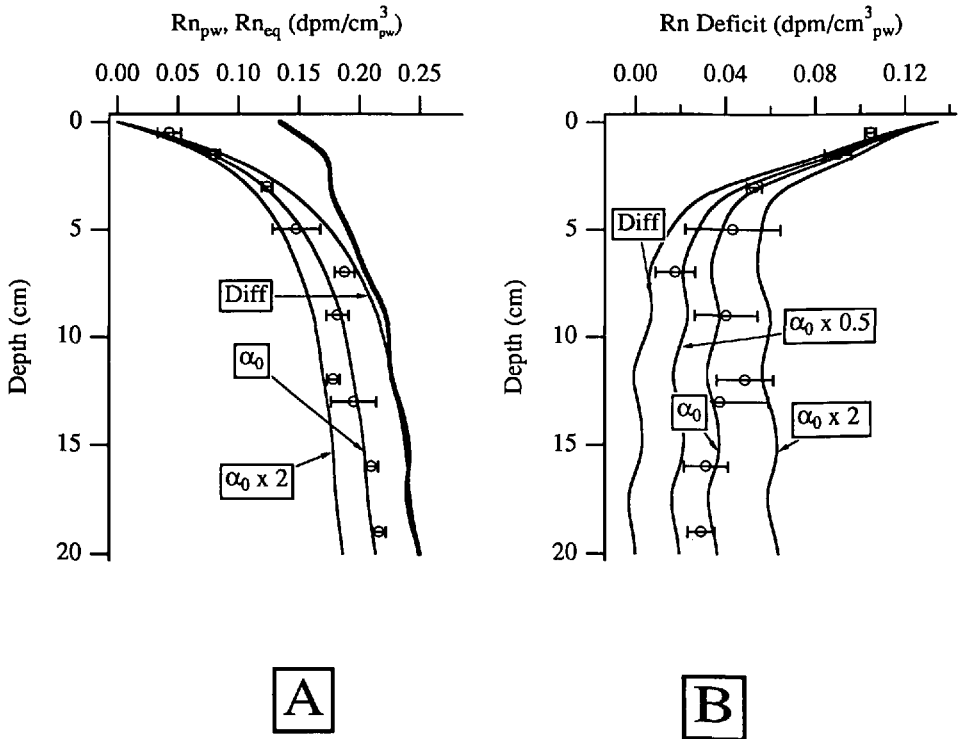
Figure 2. The sensitivity of pore water ^{222}Rn (Fig. 2A) and pore water ^{222}Rn deficit (Fig. 2B) profiles to variations in the irrigation rate parameter, α_0. The data in the figure are average pore water Rn (open symbols in Figure 2A), Rn_{eq} (thick solid line in Fig. 2A), and Rn deficit (open symbols in Fig. 2B) from cores RF1, L1, and L2. The error bars indicate both analytical uncertainties and small-scale spatial heterogeneity. The baseline α_0 value is the best-fit value for the averaged Rn and Rn_{eq} profiles.

shown at each depth represent the ranges in measured activities. Thus, they reflect small-scale spatial heterogeneity as well as analytical uncertainties. In the figure, we show the pore water Rn and Rn deficit profiles that would result from factor of 2 deviations from the best-fit α_0 value. With irrigation rates similar to those measured at this site, Rn profiles are very insensitive to changes in the irrigation rate parameter in the upper 2–3 cm of the sediment column: vertical molecular diffusion is the dominant mechanism for exchange of pore water and seawater solutes in this region of the sediment column. Below this surficial zone, pore water Rn profiles do respond measurably to variations in irrigation rates. Spatial heterogeneity and measurement uncertainties appear to limit the resolution of irrigation rates to an uncertainty of about a factor of two.

d. Irrigation rate parameter estimation procedure. We used a nonlinear least squares procedure (the Levenberg-Marquardt method) to fit the models of Eqs. 3 and 5 to

excess Br⁻ and pore water ²²²Rn activity and Rn_{eq} data. The procedure follows that of Press *et al.* (1986), except that we used numerical solutions to the differential equations as fitting functions. Except for the Br⁻ profile of core L2, we used two fitting parameters for each fit, α_0 and α_1 in equation 2. In the case of core L2, more rapid irrigation was required in the upper centimeter of the sediments; to allow this, we introduced a third irrigation rate parameter specifying the rate in the upper centimeter. Thus, by specifying the form of the depth-variation of the irrigation rate parameter as well as sediment porosity and diffusivity (Table 2), we constrained the curvature of model profiles. Within this constraint, the fitting procedure adjusted the irrigation rate parameters to optimize the fit of the model to measured concentration vs. depth profiles.

4. Results

a. Model fits to excess Br⁻ profiles. Excess Br⁻ profiles measured at the end of each incubation are shown in Figures 3A, 3B, and 3C. The cores in Figure 3A were not manipulated. Of these cores, L1 and L2 were taken in September, 1989 and incubated and sampled immediately, while cores U1 and U2 were taken in May, 1988 and sampled in August, 1988. The cores in Figure 3B were manipulated for suppression of macrofaunal activity, and no macrofauna were added after the cores were defaunated. The cores in Figure 3C were also defaunated, but after this treatment, Nephtys (cores N1 and N2) or Mediomastus (core M1) were added to them.

Each excess Br⁻ profile is compared to the diffusive profile that is predicted for the conditions of the incubation (the shaded area in each plot). Diffusion coefficients were calculated from the data of Li and Gregory (1974) and corrected for sediment tortousity and porosity by $D_{sed} = D_w\phi^2$. Two cores (D2 and U2) show no evidence of enhanced Br⁻ transport by irrigation. We applied the model of equation 3 to cores D2 and U2 with $\alpha = 0$ and the diffusion coefficient for Br⁻ as an adjustable parameter. The best-fit D_{Br} values were only 17% (core D2) and 7% (core U2) greater than the calculated values. Irrigation was somewhat more important to the core N1 Br⁻ distribution, as the best-fit D_{Br} was 27% larger than the calculated value. Cores U1, N2, and L1 required values 49–69% greater. We did not apply the diffusion-only model to cores L2, D1, and M1, whose excess Br⁻ profiles clearly cannot be explained by diffusion alone.

Fits of the irrigation model to Br⁻ profiles are shown by the solid lines in Figure 3. In most cases, the model explains the distributions well. The exceptions are two cores in which subsurface Br⁻ maxima are present: core M1 and core L2. The irrigation model is based on the assumptions that all burrows are connected to overlying seawater and that burrow water is exchanged rapidly with overlying water. Under these circumstances, if the properties of burrow walls remain constant with depth below the sediment-water interface, the principle cause of apparent subsurface irrigation rate maxima would be spatial heterogeneity. With patchy distributions of

Table 2. Model input parameters.

A. Porosity: Best-fit, a,b,c in $\phi = a + b\,e^{-cx}$

Core	a	b	c
N1	.707	.156	.0875
D1	.665	.177	.0411
M1	.645	.196	.0334
U1	.645	.248	.183
D2*	.665	.177	.0411
N2*	.707	.156	.0875
U2	.652	.228	.0822
RF1**	.707	.156	.0875
L1**	.707	.156	.0875
L2**	.707	.156	.0875

Notes: *Porosity was not measured for cores D2 and N2. Profiles from similarly treated cores were used: from core D1 for core D2; from core N1 for core N2.

**Average values measured in a set of 6 cores sampled at the study site from 1982–1984 (Martin and Sayles, 1987)

B. Incubation Parameters

Core	Thickness of incubated seds	Height of olw	Initial Br⁻ concentration	Incubation length
N1	15.5	29	8.17	1.51
D1	16	19	10.03	1.48
M1	16	30.5	7.80	1.09
U1	13	31	7.89	1.46
D2	18	19.5	9.38	1.43
N2	16	26.5	8.88	1.44
U2	18	31.5	7.52	1.55
L1	21	25	9.67	1.47
L2	22	26	10.27	0.96

Sediment thickness and overlying water height are in cm; initial Br⁻ concentration is in mmol/l; incubation length is in days.

C. Diffusivities, in water, for Rn and Br⁻ (cm²/day)

Core	D_{Br}*	D_{Rn}**
N1	1.66	1.11
D1	1.58	1.04
M1	1.67	1.12
U1	1.59	1.05
D2	1.63	—
N2	1.63	—
U2	1.63	—
RF1	—	1.05
L1	1.60	1.05
L2	1.60	1.06

Notes: *D_{Br} values based on Li and Gregory, 1975.
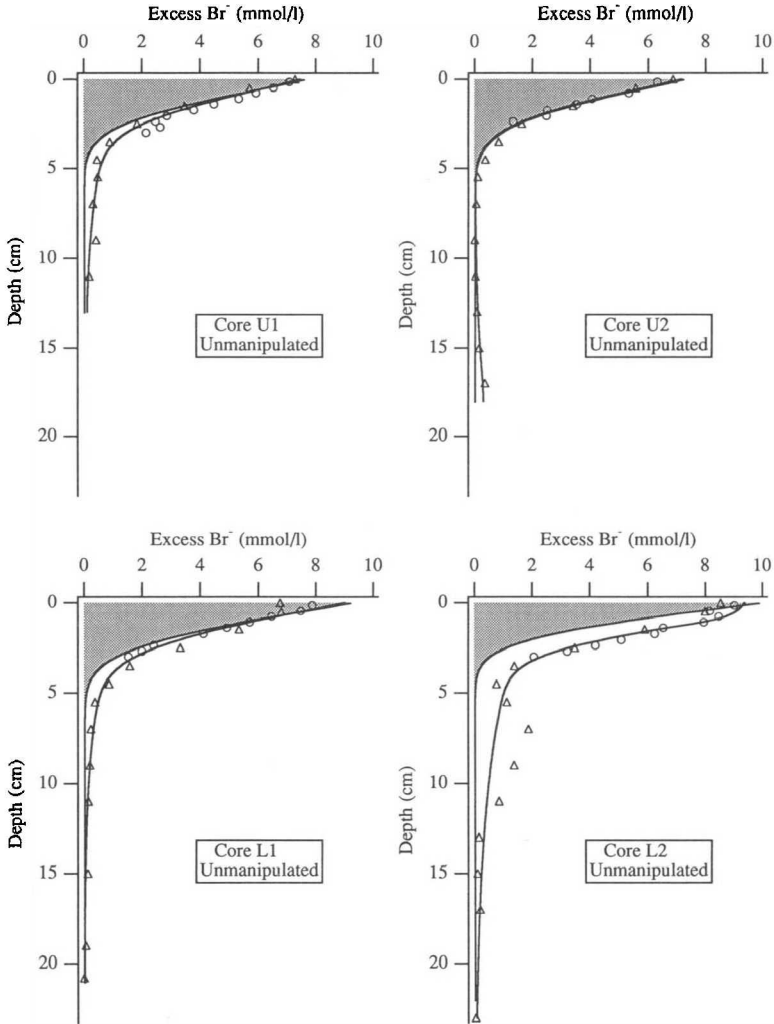**D_{Rn} values based on Broecker and Peng, 1974.

Figure 3. Excess Br⁻ profiles, measured at the end of the sediment incubations. In each graph: excess Br⁻ data are represented by open symbols, circles for the fine-interval samples taken in the upper 3 cm and triangles for the coarse-interval samples; the profile that would be produced by vertical molecular diffusion only, under the conditions of the incubation, is shown by the shaded area; and the best-fit excess Br⁻ profile, given the input data in Table 2 and using α_0 and α_1 as fitting parameters, is shown by the solid line. (A) Cores that were not manipulated; (B) Cores that were treated for suppression of macrofaunal activity, but to which no animals were added after the treatment; (C) Cores that were treated for suppression of macrofaunal activity, and to which populations of the indicated polychaete were added after the treatment.
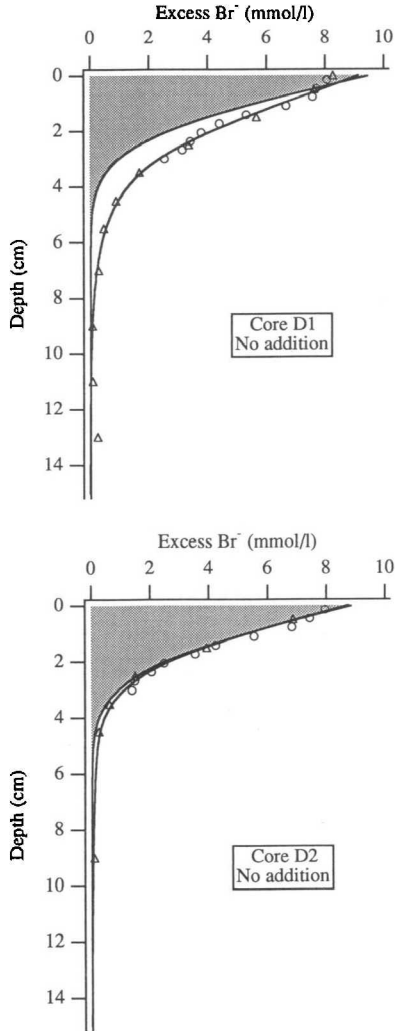
Figure 3. (Continued)

burrows, some of which are not vertical, subcores are likely to intersect burrows. When this happens, as it apparently did in the cases of Cores L2 and M1, the model cannot represent accurately the irrigation rate in the region of the maximum. In the case of core M1, the subsurface maximum appears to cause the fitting procedure to underestimate α in the region of the maximum and to overestimate the irrigation rate below the maximum; whereas the data show no detectable irrigation below 8 cm, the model fit requires that there be measurable excess Br^-.

Spatial heterogeneity may also affect the results from cores U1 and L1, but to a lesser extent. Pore water excess Br^- profiles were measured in two subcores for each core. In most cases, there is little difference between the two subcores, but in the
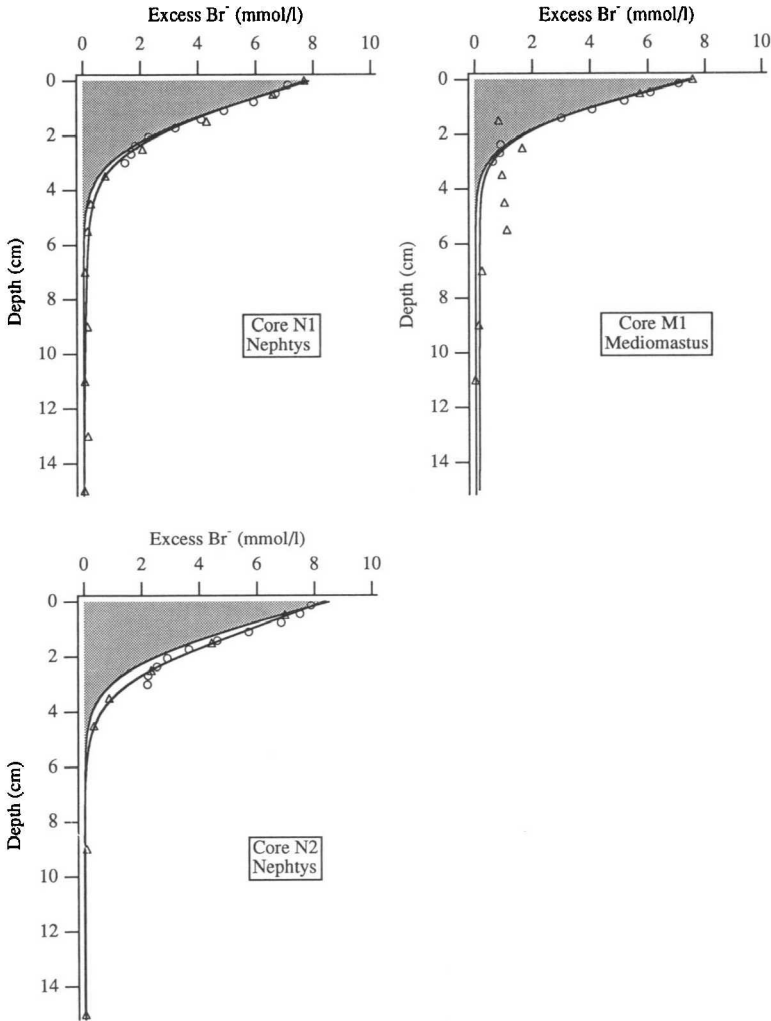
Figure 3. (Continued)

cases of cores U1 and L1, one subcore is systematically different from the other. In both cases, the model fit to the data favors the profile showing smaller excess Br⁻ concentrations; thus, the model fits may tend to underestimate irrigation rates for these cores.

b. Model fits to Rn deficit profiles. A comparison of pore water Rn deficit profiles to profiles produced by vertical molecular diffusion alone shows that there is significant irrigation over the entire length of each core (Fig. 4). Rn diffusion coefficients were estimated from the tabulation of Broecker and Peng (1974), adjusted for sediment tortuosity and porosity by $D_s = D_{sw}\phi^2$. The cores fall into two groups: the manipulated
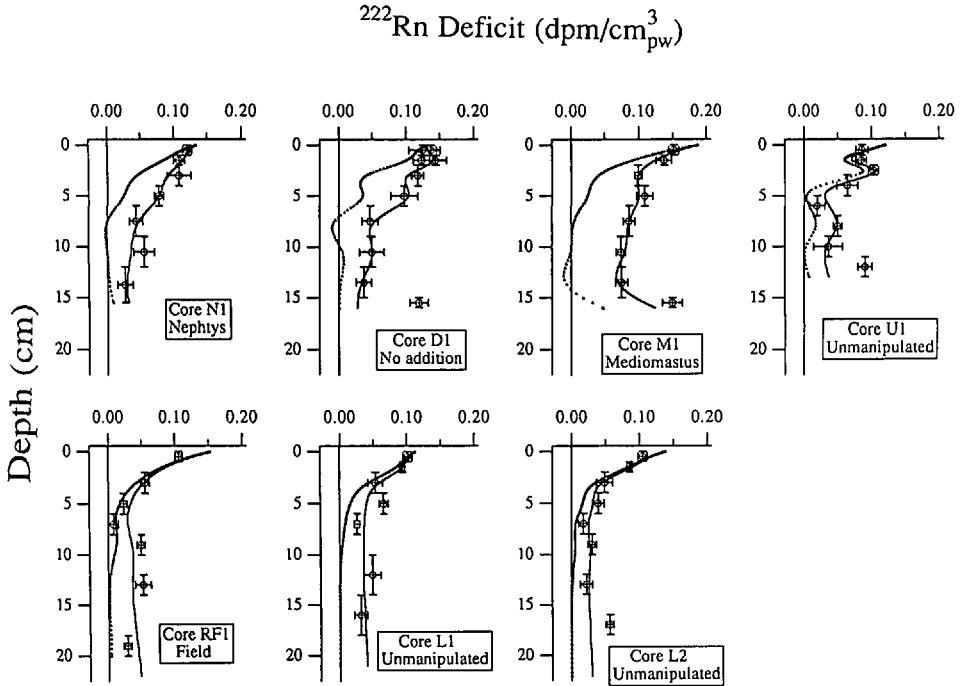
$$^{222}\text{Rn Deficit (dpm/cm}^3_{pw})$$

Figure 4. Pore water ^{222}Rn deficit profiles. In each graph: the "vertical molecular diffusion only" profile is shown by the small triangles; the best-fit Rn deficit profile, using α_0 and α_1 as fitting parameters, is shown by the solid line; and the measured values are shown by the open circles. The analytical uncertainty is shown by the horizontal error bars; the sampling interval is indicated by the vertical error bars.

cores (N1, D1, and M1), which have Rn deficits significantly larger than those that can be explained by vertical molecular diffusion alone throughout their length, and the unmanipulated cores, which only have deficits greater than those attributable to diffusion deeper than about 3 cm below the sediment-water interface. This does not indicate an absence of irrigation near the interface, but rather that pore water/ overlying water exchange due to irrigation in this region is slow relative to that due to molecular diffusion (see Fig. 2).

Core handling and sampling, as well as analytical techniques, may lead to the derivation of artificially high irrigation rates from Rn deficit profiles. Loss of Rn during sampling or overestimation of Rn_{eq} may occur. Both types of error would cause overestimates of pore water Rn deficits.

Slow Rn loss during the time the cores were maintained in the laboratory, for instance by diffusion through the walls of sediment microcosms, could cause overestimates of irrigation-based Rn deficits. We tested for this effect by measuring Rn profiles in unmanipulated cores that were treated in different ways. Core U1 was maintained in the laboratory for 3 months before the Rn profile was determined.
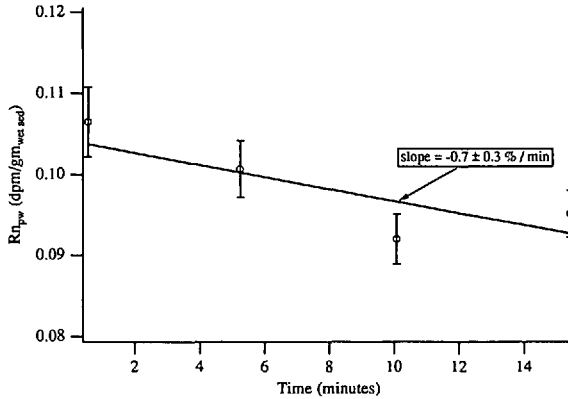
Figure 5. Loss of pore water Rn during sampling. The symbols show measurements of subsamples from the same sediment section, after the section had been exposed to air for varying times. 1 cm thick, 6.5 cm diameter sediment sections were covered with a plastic sheet between the time of removal of the previous section and sampling. After that, their tops were left open to the atmosphere while the sections were subsampled several times. The exposure time is shown on the horizontal axis. Typical exposure time for actual samples was 3 minutes.

Cores L1 and L2 were incubated in the laboratory immediately after the cores were collected. Core RF1 was not incubated; the Rn profile was determined immediately upon return of the core to the laboratory. The Rn-derived irrigation rate parameters were identical for these 4 cores, indicating that core handling was not a likely cause of the observed Rn deficits. It should be noted, however, that large Rn deficits were observed in the deepest sample in two of the cores that had been maintained in the laboratory (D1 and U1; the high deficit observed in the deep sample in core M1 is explained by the high Rn_{eq} observed in the deepest sample—see Fig. 4). These large deficits were probably artifacts of the subcoring procedure, when subcores were pulled out of the microcosms. Since Rn profiles were measured just 2–3 hours after subcoring, it is unlikely that diffusion of Rn would have allowed this artifact to affect results at shallower depths. These points were excluded from model fits for cores D1 and U1.

Rn could also be lost during sediment sampling: the sediment sections were partially open to air for a brief period of time (about 3 minutes) during sampling. We tested for loss of Rn from pore waters during this exposure. It does occur, at a rate of about 1% per minute (Fig. 5). The increase in radon deficits due to this loss would be most important in deeper samples, where deficits are smallest. Below 10 cm depth, the increase in the deficit would be about 0.01 dpm/cm^3_{pw}, an amount equivalent to less than 25 ± 10% of the observed deficits.

Finally, it has been reported that the measurement of Rn_{eq} using sediments that have been slurried previously in order to measure pore water Rn activities leads to overestimates of Rn_{eq} and deficits (Smethie *et al.,* 1981; Berelson *et al.,* 1982). In

Table 3. Comparison of Rn_{eq} values determined on samples that either had or had not been slurried previously.

Sample	Slurried	Not Slurried	ΔRn_{eq}
S1	0.143 ± .004	0.132 ± .004	0.011 ± .006
S2	0.137 ± .003	0.129 ± .004	0.008 ± .006
S3	0.123 ± .004	0.123 ± .004	0.000 ± .006

Units: $dpm/gm_{wet\,sed}$.

earlier work in Buzzards Bay, we found no evidence for this effect (Martin and Sayles, 1987). We have carried out additional tests on 3 samples taken during this study (Table 3). Previously slurried samples gave higher Rn_{eq}, by 0–11% of the measured value. This overestimate, if real, could account for 8–23% of the Rn deficits observed below 10 cm depth.

In summary, we have measured significant Rn deficits through the entire lengths of all the cores we have analyzed, but additional experiments showed that sampling and analytical uncertainties may have led to some overestimate of deep Rn deficits. However, the effects of possible artifacts would have to be important only deep in the sediments, as Rn deficits equal to the smallest expected deficits (those caused by vertical molecular diffusion alone) were often observed in the upper 5 cm of the sediments. If these overestimates occurred, they could account for up to 50% of the measured Rn deficits below 10 cm depth.

5. Discussion

a. The in situ Br⁻ profile. Previous studies of the sedimentary geochemistry of Br have shown that, although Br is quasi-conservative in seawater (Morris and Riley, 1966), its sedimentary concentration is closely correlated to that of organic carbon (Price and Calvert, 1977; Pedersen and Price, 1980). Thus, it must be released during organic matter oxidation. Fischer *et al.* (1986) have shown, by comparing the rain rate of Br to the sea floor and Br accumulation rates in sediments of the eastern Pacific, that less than 2% of the solid phase Br reaching the sea floor is preserved. However, the Br/C ratio in sedimentary organic matter is less than 2×10^{-3} mol Br/mol C. In some cases, the Br/C_{org} ratio in sediments decreases somewhat with depth, but the decreases that have been observed are always less than a factor of two; thus, Br is released approximately in constant proportion to C_{org}. The annually averaged organic carbon degradation rate at our study site is about 600 μmol C/cm^2/yr (McNichol *et al.*, 1988), which implies a Br⁻ flux of only about 1 μmol/cm^2/yr. Further, observed increases in dissolved inorganic carbon concentrations in Buzzards Bay pore waters (McNichol *et al.*, 1988), coupled with the fact that the diffusivity of Br⁻ is about 70% greater than that of HCO_3^-, indicate that organic matter degradation will increase the pore water Br⁻ concentration by only about 0.2%. Two *in situ* Br⁻ profiles, measured in September, 1989, confirm this reasoning. One profile was measured immediately
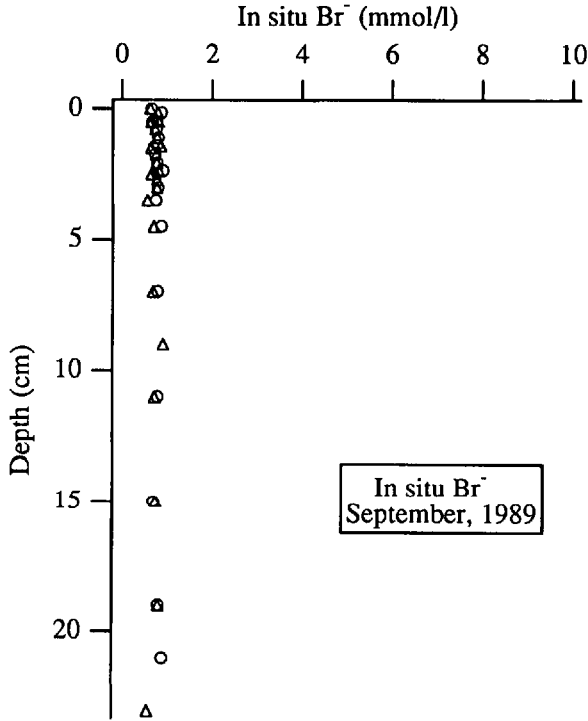
Figure 6. The concentration of Br⁻ in the pore waters of two unspiked cores from the study site.

after collection of the core, while the other was measured after the core had been incubated in the laboratory. The profiles show no trend in [Br⁻] with depth below the sediment-water interface (Fig. 6); the small variations in concentration are due to analytical uncertainties, which are important because the *in situ* Br⁻ concentration is near the detection limit of the analytical procedure. The Br⁻:Cl⁻ ratio, 0.00158 ± 0.00010 mol Br⁻/mol Cl⁻, is identical to the ratio reported for seawater (Morris and Riley, 1966).

A second potential problem arises from the fact that the Br/C ratio in sedimentary organic matter is larger than the corresponding ratio in freshly produced organic matter (Price and Calvert, 1977; Mayer *et al.,* 1981). A possible explanation for this enrichment is that it is due to the uptake of diagenetically released Br by surficial sediment organic matter. This mechanism has been invoked to explain iodine enrichments in surficial sediment organic matter (Price and Calvert, 1977), but, because Br⁻ is much less readily oxidized than I⁻ in seawater, it is not likely to be important for Br; rather, Br is probably enriched because it is not bound by the most labile components of organic matter, which are degraded first (Mayer *et al.,* 1981). Thus, although we cannot rule out the uptake of Br⁻ by sedimentary organic matter during the course of our experiments, existing data indicate that it is not likely to

occur. Reversible uptake would lead to apparent diffusion coefficients for Br^- that are smaller than molecular diffusion coefficients. We did not observe such low diffusivities; rather, the smallest apparent diffusivities consistent with our data were 7% and 17% larger than estimated molecular diffusivities.

b. NaBr addition and sedimentary respiration rates. In evaluating the Br^- tracer addition method as a means of monitoring solute transport rates in sediments, it is important to consider whether the addition affects the rates of metabolic processes in the sediments. To examine this possibility, four cores were incubated within a week of collection in September, 1989. NaBr was added to three of them, but not to the fourth. The sedimentary O_2 demand in the three cores to which NaBr was added was 19.4 ± 0.2 mmol/m^2/day; the dissolved O_2 flux into the no-addition core was 23 mmol/m^2/day. The dissolved inorganic nitrogen fluxes from the NaBr-addition cores were 3.4 ± 0.3 mmol/m^2/day, compared to 2.74 from the no-addition core. It is unlikely that these differences are significant, as they are smaller than the ranges observed among sets of cores undergoing similar treatments (Banta, 1991). Although limited, this test indicates that Br^- addition had little or no effect on sedimentary metabolic rates.

c. NaBr addition and irrigation rates. Irrigation rate parameters from different cores and different measurement methods are compared in Figures 7A and 7B. We have noted several sources of uncertainty in the irrigation rate parameters derived from our excess Br^- and Rn deficit profiles. The sensitivity of the Br^- profiles to variations in α_0 and α_1 (Fig. 1) is limited by the short durations of the incubations, made necessary by the rapid respiration rates in these nearshore sediments. The limitations of the Rn deficit profiles are due to sampling and analytical uncertainties, which may cause overestimates of irrigation rate parameters. In addition, the α_0 and α_1 values derived from model fits to the data may not be entirely independent of each other: in the region of our greatest sampling density (0–5 cm below the sediment-water interface), variations in α_0 and α_1 cause qualitatively similar variations in concentration vs. depth profiles. For these reasons, we probably only know α_0 and α_1 values (Table 4) to within a factor of 2. Therefore, in order to compare irrigation rate parameters from different cores and different measurement methods, we have averaged α values over 5 cm intervals of the sediment column.

   Irrigation rates were determined using Rn deficit profiles in three cores taken in September, 1989. NaBr was added to two of these cores, which were then incubated (cores L1 and L2). No NaBr was added to the third core; it was sampled for pore water Rn as soon as it was returned to the laboratory (core RF1). The irrigation rates measured using Rn deficit profiles in these three cores are identical. Thus, in this limited test, there was no evidence for an effect of NaBr addition on sediment irrigation rates.
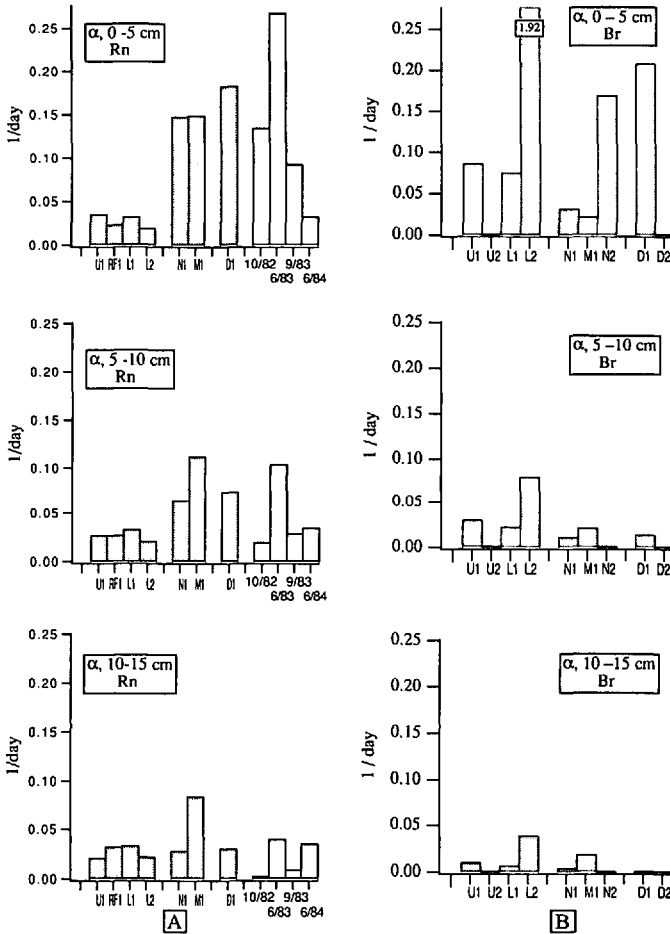
Figure 7. Irrigation rates, integrated over 5 cm intervals of the sediment column, based on the best-fit α_0 and α_1 values. (A) Irrigation rates derived from pore water Rn deficit profiles. The figure includes results from this study (filled bars) and from the study of Martin and Sayles (1987) (open bars). (B) Irrigation rates derived from pore water excess Br⁻ profiles, measured at the end of 1–1.5 day sediment incubations. Note that the value for core L2, 0–5 cm, is well off scale.

There is also some, less direct evidence that NaBr additions did not affect irrigation rates. We measured irrigation rates using Rn deficit data in cores taken from the same site in Buzzards Bay from 1982–1984 (Martin and Sayles, 1987). The range of rates measured, and their variability with depth below the sediment-water interface, were very similar to the ranges observed during this study (Fig. 7A). With the exception of core L2, whose excess Br⁻ profile implies an extremely rapid irrigation rate in the surficial sediments ($\alpha = 2$ day⁻¹: Fig. 7B), the range of irrigation rates in the upper 5 cm is about 0.03–0.25 day⁻¹ for both studies. In general, the irrigation rate parameters based on both studies decrease with increasing depth

Table 4. Best-fit values of the irrigation parameters, α_0 and α_1

Core	$\alpha_0(day^{-1})$	$\alpha_1(cm^{-1})$
(A) Fits to Br^- profiles		
N1	0.051	0.21
D1	0.60	0.54
M1	0.023	0.018
U1	0.14	0.21
N2	0.82	0.97
L1	0.13	0.24
L2*	0.23	0.14
(B) Fits to ^{222}Rn deficit profiles		
N1	0.22	0.17
D1	0.28	0.18
M1	0.17	0.057
U1	0.041	0.054
RF1	0.021	−0.037
L1	0.033	−0.002
L2	0.019	−0.012

*For this core, α_0 applies at depth $x = 1$ cm. Above $x = 1$ cm, α is constant at 6.86 day^{-1}.

below the sediment-water interface; very little irrigation is apparent from the excess Br^- profiles below 10 cm depth. The exceptions to the general trend of decreasing α with increasing depth are the Rn-based values from the unmanipulated cores (U1, RF1, L1, and L2) and from one of the cores from the earlier study (the 6/84 core). These Rn deficit profiles are consistent with relatively slow irrigation rates that are constant with depth.

d. Comparison of irrigation rate parameters from excess Br^- and Rn deficit profiles. In comparing values of the irrigation rate parameters determined from profiles of the two tracers, differences in their diffusion coefficients must be taken into account: according to the irrigation model, the step which limits solute exchange between seawater and pore water via burrows is diffusion across the burrow walls. The diffusion coefficient of Br^- in water is 50% larger than that of Rn. Thus, to compare α values in Figure 7A (derived from Rn deficits) to those in Figure 7B, the Rn values should be increased by 50%. The range of values in the 0–5 cm interval of the sediment column is similar for the two tracers; below that depth, most of the values derived from Rn deficit profiles are significantly larger than those based on excess Br^- profiles. There are several possible explanations for these differences. First, Rn deficits below 5 cm may be overestimated by amounts of a few % up to 50%. If the higher estimates of the uncertainty are correct, then uncertainties in the Rn analysis could explain a large amount of the differences. Second, the Rn and Br^- profiles are determined by events occurring over quite different time scales: the 1.5 day length of the incubations for Br^-, two to three weeks for Rn. If the incubating procedure

causes a change in the activities of infauna or if their activities vary sporadically with time for other reasons, this change would be reflected in differences between irrigation rates derived from Rn deficits and excess Br⁻ profiles. Finally, it has been shown that the diffusion of Br⁻ through the linings of animal burrows is hindered relative to that of small cations such as NH_4^+ (Aller, 1983). As we will show below, it is likely that, among the more abundant infauna in our experimental system, *Nephtys incisa* was most important in influencing irrigation rates. *Nephtys* does not have lined burrows. Nonetheless, if a significant fraction of the burrows in the sediments we have analyzed are lined, the resultant hindrance to diffusion of anions would help to explain the observed differences between irrigation rates based on Br⁻ and Rn deficit profiles.

Despite the differences in absolute irrigation rates from the two methods, there are several important similarities. The cores for which rates were determined using both tracers are N1, D1, M1, and U1 in 1988, and L1 and L2 in 1989. Both methods show that, among the 1988 cores, core D1 had the most rapid irrigation rate in the surface interval, and the rate which decreased most sharply with increasing depth. Cores N1 and M1 gave quite different absolute rates for the two tracers. For each tracer, they yielded similar rates in the surface interval, but, while core M1 showed little decrease in irrigation rate with depth, the rate for core N1 decreased markedly. It should be noted, however, that because of the subsurface maximum in the excess Br⁻ profile for core M1, the irrigation model underestimates the rate in the 5–10 cm interval and overestimates the rate below 10 cm (see the model fit to the data in Figure 3C). If this overestimate is taken into account, then the unmanipulated core (#U1) shows the smallest decrease in irrigation rate with depth, based on both the Rn and Br⁻ measurements. In 1989, the Br⁻ profile for core L2 shows much more rapid irrigation in the surface interval than does Rn deficit. The difference is considerably larger than can be accounted for by any of the uncertainties we have discussed: it must be due to spatial heterogeneity. Nonetheless, the unmanipulated cores of the 1988–89 study, taken together, have a common feature. With the exception of the overestimated irrigation rate below 10 cm for core M1, the unmanipulated cores show the smallest decreases in irrigation rates from 5–15 cm, based on both the Rn deficit and Br⁻ tracer methods.

e. Irrigation rates and macrofaunal abundance. The defaunation procedure used to treat the manipulated cores during the 1988 study was effective at removing animals living near the sediment surface. While *Mediomastus* and *Nucula* were abundant in unmanipulated cores, they were almost completely absent in all the treated cores except #M1, to which *Mediomastus* were added after the defaunation procedure. The result of the treatment was that the unmanipulated cores had the most abundant and diverse macrofauna (Fig. 8). We have noted that there are differences in irrigation rates between the manipulated and unmanipulated cores. The Br⁻ results
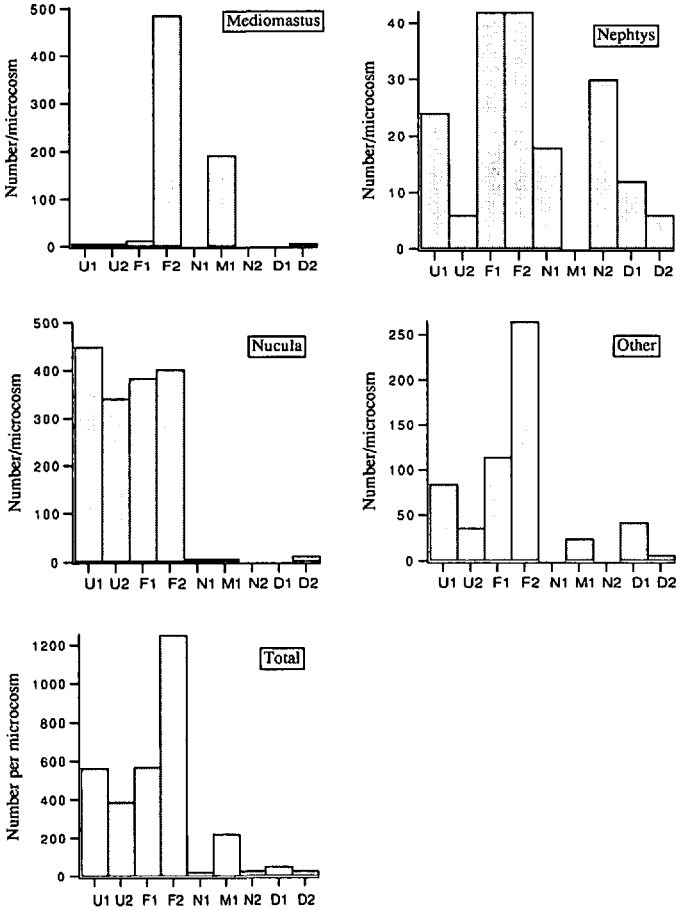
Figure 8. Macrofaunal abundances. The subcores for determination of macrofauna represent one-sixth of the area of the sediment core from which they were taken. Thus, the numbers on the vertical axis are 6 times the actual number identified. The surface area of the sediment subcores was 0.00312 m², that of the microcosms themselves 0.0191 m². In 1989, macrofaunal abundances were not determined on the incubated cores, L1 and L2. Cores F1 and F2 were taken from the study site at the same time as L1 and L2.

show that the unmanipulated cores had the most rapid irrigation rates below the surface 5 cm interval (as we noted above, core M1 is an exception to this generalization). The Rn results do not show this difference in irrigation rates, but they do yield irrigation rates that decrease much more slowly with increasing depth in the unmanipulated cores than in the manipulated ones.

Nephtys is the largest animal and the most active and deepest burrower among the abundant infauna in the fine-grained sediments of Buzzards Bay. Adult *Nephtys* at the study site were generally 1–3 cm in length, occasionally reaching 5 cm. The size range of juveniles was generally 0.2–1 cm. *Mediomastus* were considerably smaller,
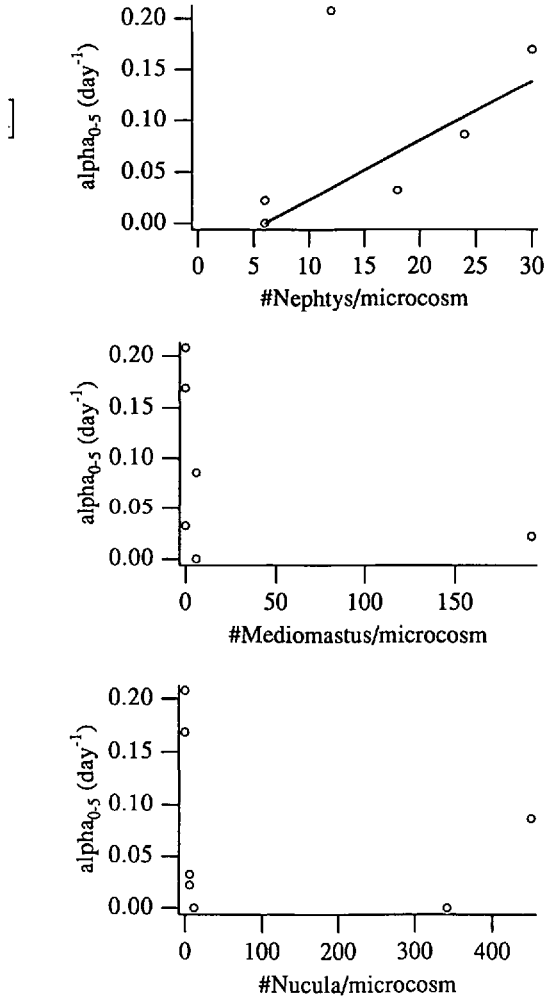
Figure 9. Correlations between the irrigation rate parameter measured in the 0–5 cm interval using the Br⁻ tracer method and macrofaunal abundances. Figure 9A: α vs. *Nephtys* abundance; Figure 9B: α vs. *Mediomastus* abundance; Figure 9C: α vs. *Nucula* abundance. The line in Figure 9A is the best-fit, if core D1 is excluded (core D1 is the point at #*Nephtys* = 12, α = 0.208). The correlation coefficient for the α vs. *Nephtys* data is .84 if core D1 is excluded, and .35 if core D1 is included.

with juveniles less than 0.2 cm in length and adults only reaching a maximum size of 1 cm. *Nucula* were generally 0.05–0.2 cm across. The populations examined during this study were dominated by animals at the smaller end of the size spectrum.

It is not surprising, given *Nephtys'* greater size and activity, that *Nephtys* numbers are more closely correlated to measured irrigation rates than are the numbers of the other macrofauna studied (Fig. 9). The most rapid rate was measured in core L2, which was taken during September, 1989 and incubated immediately after core

recovery: at this time, field measurements (F1 and F2) showed Nephtys abundances greater than in any of the other incubated cores. Cores D2 and U2 showed no evidence of irrigation in their Br⁻ profiles. Only a single *Nephtys* was counted in the subcores used for macrofaunal abundance measurements in each of these cores (extrapolating to 6 individuals per microcosm). Cores with intermediate irrigation rates—U1, N1, N2, and D1—had intermediate *Nephtys* abundances. No other correlations of irrigation rates with macrofaunal abundance are visible. The correlations of irrigation rates with *Nephtys* abundance are not apparent in the results from Rn deficit profiles, but it should be noted that the range of *Nephtys* abundances in cores for which Rn deficits were determined was smaller than that in cores for which excess Br⁻ profiles were measured. The rapid irrigation rate in the 0–5 cm interval in core L2 was not recorded in the Rn deficit profile; and Rn profiles were not measured in the two cores with low *Nephtys* abundances and no discernible irrigation (cores D2 and U2).

6. Conclusions

We have used two methods to determine sediment irrigation rates in a set of cores taken from the fine-grained sediments of Buzzards Bay, MA. The most important difference between the methods is that, while the Br⁻ tracer method requires a sediment incubation and averages irrigation rates over time and space scales that are determined by the length of the incubation, the Rn deficit method averages events occurring over a two to three week period. This characteristic of the Br⁻ tracer method may be particularly important for the measurement of irrigation rates during benthic flux chamber deployments, as the derived rates apply specifically to the conditions of the experiment.

Our experiments indicate that NaBr meets several essential criteria for an irrigation rate tracer. Pore water profiles of Br⁻ indicate that natural Br cycling does not alter concentrations enough to affect tracer experiments, at least in the near-shore sediments where we carried out our experiments. Neither sedimentary metabolic activities nor irrigation rates appeared to be affected by the addition of NaBr, which elevated the Br⁻ concentration in the water overlying the sediments by a factor of ten.

There were significant differences between the irrigation rates determined on the same cores using the two methods: rates determined from Rn deficits were faster at depths greater than 5 cm below the sediment-water interface. These differences could be caused by several factors: by the different scales of spatial and temporal averaging; by differences in the permeability of burrow walls to Br⁻ and Rn; or by uncertainties in pore water Rn sampling and analysis that may lead to overestimates of irrigation rates. Despite these differences in rates, the patterns of variation of rates with depth below the sediment-water interface in individual cores and between cores were generally similar for both measurement techniques.

REFERENCES

Aller, R. C. 1980a. Diagenetic processes near the sediment-water interface of Long Island Sound. I, *in* Decomposition and Nutrient Element Geochemistry (S, N, P), B. Saltzman, Academic Press, 237–349.

—— 1980b. Quantifying solute distributions in the bioturbated zone of marine sediments by defining an average microenvironment. Geochim. Cosmochim. Acta, *44,* 1955–1965.

—— 1982. Carbonate dissolution in nearshore terrigenous muds: the role of physical and biological reworking. J. Geol., *90,* 79–95.

—— 1983. The importance of the diffusive permeability of animal burrow linings in determining marine sediment chemistry. J. Mar. Res., *41,* 299–322.

Aller, R. C. and J. Y. Yingst. 1985. Effects of the marine deposit-feeders *Heteromastus filiformis* (Polychaeta), *Macoma Baltica* (Bivalvia), and *Tellina texana* (Bivalvia) on averaged sedimentary solute transport, reaction rates, and microbial distributions. J. Mar. Res., *43,* 615–645.

Aller, R. C., J. Y. Yingst and W. J. Ullman. 1983. Comparative biogeochemistry of water in intertidal *Onuphis* (polychaeta) and *Upogebia* (crustacea) burrows: temporal patterns and causes. J. Mar. Res., *41,* 571–604.

Archer, D. and A. Devol. 1991. Benthic oxygen fluxes on the Washington shelf and slope: a comparison of microelectrode and chamber flux measurements. Limnol. Oceanogr., (in press).

Banta, G. T. 1991. Decomposition and nitrogen cycling in coastal marine sediments—controls by temperature, organic matter inputs, and benthic macrofauna. PhD. Thesis, Boston University.

Bender, M., W. Martin, J. Hess, F. Sayles, L. Ball and C. Lambert. 1987. A whole-core squeezer for interstitial pore-water sampling. Limnol. Oceanogr., *32,* 1214–1225.

Berelson, W. M., D. E. Hammond and K. S. Johnson. 1987. Benthic fluxes and the cycling of biogenic silica and carbon in two southern California borderland basins. Geochim. Cosmochim. Acta, *51,* 1345–1363.

Bishop, D. W. 1952. Respiration and metabolism, *in* Comparative Animal Physiology, C. L. Prosser, ed. W.B. Saunders, Philadelphia, 209–289.

Boudreau, B. P. 1984. On the equivalence of nonlocal and radial-diffusion models for porewater irrigation. J. Mar. Res., *42,* 731–735.

Broecker, W. S. and T.-H. Peng. 1974. Gas exchange rates between air and sea. Tellus, *26,* 21–35.

Brownawell, B. J. 1986. The role of colloidal organic matter in the marine geochemistry of PCBs. PhD Thesis, Woods Hole Oceanographic Institution/Massachusetts Institute of Technology Joint Program in Oceanography, 318 pp.

Christensen, J. P., A. H. Devol and W. M. Smethie, Jr. 1984. Biological enhancement of solute exchange between sediments and bottom water on the Washington continental shelf. Cont. Shelf Res., *3,* 9–23.

Crank, J. 1975. The Mathematics of Diffusion, Oxford University Press, Oxford.

Emerson, S., R. Jahnke and D. Heggie. 1984. Sediment-water exchange in shallow water estuarine sediments. J. Mar. Res., *42*, 709–730.

Farrington, J. W., S. M. Henrichs and R. Anderson. 1977. Fatty acids and ^{210}Pb geochemistry of a sediment core from Buzzards Bay, MA. Geochim. Cosmochim. Acta, *41*, 289–296.

Fischer, K., J. Dymond, M. Lyle, A. Soutar and S. Rau. 1986. The Benthic cycle of copper: Evidence from sediment trap experiments in the eastern tropical North Pacific Ocean. Geochim. Cosmochim. Acta, *50*, 1535–1543.

Grassle, J. P. and J. F. Grassle. 1984. The utility of studying the effects of pollutants on single species populations in benthos of mesocosms and coastal ecosystems, *in* Concepts in Marine Pollution Measurements, H. White, ed., Maryland Sea Grant Program, College Park, MD, 621–642.

Hammond, D. E., C. Fuller, D. Harmon, B. Hartman, M. Korosec, L. G. Miller, R. Rea, S. Warren, W. Berelson and S. W. Hager. 1985. Benthic fluxes in San Francisco Bay. Hydrobiologia, *129*, 69–90.

Key, R. M., R. L. Brewer, J. H. Stockwell, N. L. Guinasso, Jr. and D. R. Schink. 1979a. Some improved techniques for measuring radon and radium in marine sediments and in seawater. Mar. Chem., *7*, 251–264.

Key, R. M., N. L. Guinasso, Jr. and D. R. Schink. 1979b. Emanation of Radon-222 from marine sediments. Mar. Chem., *7*, 221–250.

Li, Y.-H. and S. Gregory. 1974. Diffusion of ions in sea water and in deep-sea sediments. Geochim. Cosmochim. Acta, *38*, 703–714.

Luedtke, N. A. and M. L. Bender. 1979. Tracer Study of sediment-water interactions in estuaries. Estuar. Coastal Mar. Sci., *9*, 643–651.

Martin, W. R. and F. L. Sayles. 1987. Seasonal cycles of particle and solute transport processes in nearshore sediments: Rn-222/Ra-226 and Th-234/U-238 disequilibrium at a site in Buzzards Bay, MA. Geochim. Cosmochim. Acta, *51*, 927–943.

Mathieu, G. G., P. E. Biscaye, R. A. Lupton and D. E. Hammond. 1988. System for measurement of ^{222}Rn at low levels in natural waters. Health Physics, *55*, 989–992.

Mayer, L. M., S. A. Macko, W. H. Mook and S. Murray. 1981. The distribution of bromine in coastal sediments and its use as a source indicator for organic matter. Org. Geochem., *3*, 37–42.

McNichol, A. P., C. Lee and E. R. M. Druffel. 1988. Carbon cycling in coastal sediments: 1. A quantitative estimate of the remineralization of organic carbon in the sediments of Buzzards Bay, MA. Geochim. Cosmochim. Acta, *52*, 1531–1543.

Moore, J. R. 1963. Bottom sediment studies, Buzzards Bay. J. Sed. Petr., *33*, 511–558.

Morris, A. W. and J. P. Riley. 1966. The bromide/chlorinity and sulphate/chlorinity ratio in sea water. Deep-Sea Res., *13*, 699–705.

Pedersen, T. F. and N. B. Price. 1980. The geochemistry of iodine and bromine in sediments of the Panama Basin. J. Mar. Res., *38*, 397–411.

Press, W. H., B. P. Flannery, S. A. Teukolsky and W. T. Vetterling. 1986. Numerical Recipes: The Art of Scientific Computing. Cambridge, U.K., Cambridge University Press.

Price, N. B. and S. E. Calvert. 1977. The contrasting geochemical behaviours of iodine and bromine in recent sediments from the Namibian shelf. Geochim. Cosmochim. Acta, *41*, 1769–1775.

Sanders, H. L. 1958. Benthic studies in Buzzards Bay I. Animal-sediment relationships. Limnol. Oceanogr., *3*, 245–258.

—— 1960. Benthic studies in Buzzards Bay III. The structure of the soft bottom community. Limnol. Oceanogr., *5*, 138–150.

Smethie, W. M., C. A. Nittrouer and R. F. L. Self. 1981. The use of Radon-222 as a tracer of sediment irrigation and mixing on the Washington continental shelf. Mar. Geol., *42,* 173–200.
Whitlatch, R. B., L. F. Boyer, H. L. Sanders and G. Hampson. Station R revisited: Long-term persistence of a subtidal benthic community. (unpubl. ms.)