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BENTHIC FLUX STUDIES IN NARRAGANSETT BAY

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ABSTRACT. Work reported here on the methodology of determining metal and nutrient fluxes in nearshore sediments shows that consistent results are obtained from static and flow-through laboratory experiments as well as *in situ* belljar experiments. Fluxes have been measured at four sites in Narragansett Bay and one site in nearby offshore waters. At sites without a vigorous macroinfauna, the measured fluxes agree well with diffusive fluxes calculated from pore water concentration gradients. Fluxes of $PO_4^{\equiv}$ and NH_3 are much greater at the polluted, urban head of the Bay than at the more pristine sites in the center; SiO_2 and Mn fluxes show little geographic variability. Mn fluxes are far higher in the summer than in the fall. Ni, Cu, and Cd fluxes are uniformly negligible, reflecting the low concentrations of these metals in anoxic sediment pore waters.

INTRODUCTION

In a companion paper (Elderfield and others, 1981), we have described the interstitial-water chemistry of sediments from Narragansett Bay, R.I. and discuss the chemical diagenesis of nutrients and metals. Our analyses show that the interstitial-water chemistry exhibits compositional variations typical of reducing sediments. TCO_2 and sulphide increase and sulphate decreases in interstitial waters relative to bottom waters. Ammonia increases, and phosphate rises to levels much higher than bottom-water values. Changes in total iodine concentrations parallel those of TCO_2. Manganese and iron concentrations also rise to high levels but nickel, copper, and cadmium decrease in interstitial waters relative to bottom waters.

This contrast between the chemistry of interstitial waters and overlying waters will promote a benthic flux of chemicals into the Bay waters or into the sediments. In this paper we give estimates of the magnitudes of the benthic fluxes at the sites where interstitial-water studies were performed. We discuss the spatial and seasonal variations in fluxes and summarize their contribution to the mass balance for the Bay.

EXPERIMENTAL PROCEDURES

The locations of the study sites are shown in figure 1. These are described by Elderfield and others (1981) except for the Ohio Ledge (OL) site which is close to and similar in character to the Rumstick Neck site.

Direct measurements of benthic fluxes were obtained using two different techniques. First, analyses were made of samples collected from *in situ* bell-jar experiments similar to those previously performed at the extensively studied Jamestown North site by Hale (ms), Graham, Bender, and Klinkhammer (1976), Nixon, Oviatt, and Hale (1976), McCaffrey and others (1980), and Bender, McCaffrey, and Cullen (ms). In this technique, PVC bell-jars, each covering an area of 0.25 m^2 and enclosing

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27 l of water, are placed over the sediment. Samples are removed from the chambers at the start of each experiment and 3 hrs later, and benthic fluxes are calculated from the concentration changes. Nutrient fluxes were measured in six replicate experiments over the period 1975-1976, two replicates in January, and four replicates in July-August (table 1). Manganese fluxes were measured in 8 duplicate experiments over the same period, 5 in January-February, 2 in July, and 2 in September-October (table 2). These supplemented the summer flux measurements of nutrients (McCaffrey and others, 1980) and manganese (Graham,

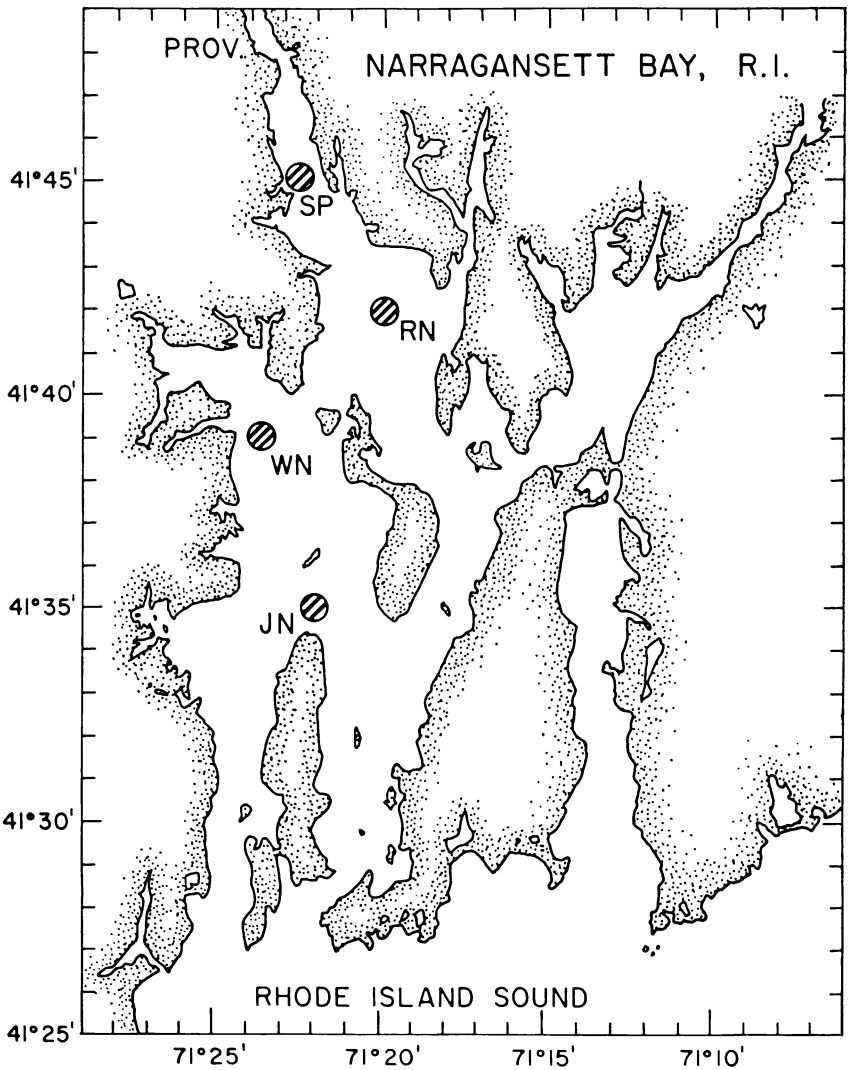

Fig. 1. Map of Narragansett Bay showing locations of sampling sites. SP = Sabin Point; RN = Rumstick Neck; OL = Ohio Ledge; WN = Warwick Neck; JN = Jamestown North; Brenton Reef (not shown) is at 41°24'N, 71°22'W.

TABLE 1

In-situ flux data: ammonia, phosphate, and silica

Site/date*		Flux (μmoles/cm^2/day) NH_3	PO_4^{3-}	H_4SiO_4
SABIN POINT				
8.19.1975	1.	1.4	0.44	—
	2.	0.8	0.71	0.5
	3.	0.7	0.77	0.3
	4.	1.8	0.31	1.7
		1.2 ± 0.5	0.56 ± 0.22	0.83 ± 0.76
1.12.1976	1.	0.18	0.05	0.1
	2.	—	0.12	0.1
		0.18	0.09	0.1
7.6.1976	1.	0.46	0.05	—
	2.	—	0.12	—
		0.46	0.09	—
RUMSTICK NECK				
8.26.1975	1.	0.30	0.06	0.27
	2.	0.76	0.04	0.90
	3.	0.98	0.17	1.70
	4.	0.56	0.08	0.89
		0.65 ± 0.29	0.09 ± 0.06	0.94 ± 0.59
JAMESTOWN NORTH				
Summer 1975**		0.27 ± 0.08	0.07 ± 0.02	1.2 ± 0.20
1.20.1976	1.	0.028	0.01	0.1
	2.	0.027	0.00	0.1
		0.028	0.01	0.1
7.13.1976	1.	0.14	0.04	—
	2.	0.44	0.06	—
		0.29	0.05	—

* Numbers after each date refer to replicate samples.
** From data of McCaffrey and others (1980).

TABLE 2

In-situ flux data: manganese

Site/date*	Flux(μmoles/cm^2/day) 1	2
SABIN POINT		
10.7.1975	0.055	0.073
12.16.1975	0.035	0.003
1.27.1976	0.007	0.002
OHIO LEDGE		
2.24.1976	0.005	0.005
WARWICK NECK		
9.9.1976	0.023	0.020
JAMESTOWN NORTH		
summer 1975**	0.049 ± 0.018	
12.10.1975	0.002	0.026
1.20.1976	0.002	0.010
7.13.1976	0.055	0.073

* Numbers 1 and 2 refer to duplicate samples.
** From data of McCaffrey and others (1980).

Bender, and Klinkhammer, 1976) made at the Jamestown North site during 1975-76.

Second, measurements were made using box cores and tube cores collected in 1977 (tables 3 and 4) which were incubated in the laboratory. Divers inserted the box corers (of rectangular or circular cross section) into the sediment to achieve a 50 percent penetration so that a sediment column of 10 to 20 cm was collected (surface area 255 or 270 cm^2) together with an overlying-water volume of 3 to 4 l. Similarly, the tube corers sampled 10 to 30 cm of sediment (surface area 42-125 cm^2) and 0.5 to 0.7 l of water. Corers containing sediment and supernatant water were transferred from holding tanks on board ship to an aquarium tank at laboratory temperature (20°C), which is similar to the summer temperature of the bottom water (fig. 8). After approx 1 hr the supernatant was very carefully removed using a peristaltic pump and replaced with fresh bottom water. We did this because nutrient concentrations in the supernatant water sometimes built up to abnormally high values during transport of cores to the laboratory. From this stage and throughout the experiments each supernatant was oxygenated by blowing air over the water surface. The cores were allowed to stand overnight, and the supernatant was again replaced with bottom water and was allowed to stand for

TABLE 3

Laboratory-incubated flux measurements: ammonia, phosphate, and silica

Site/date/core no.*		Flux (μmoles/cm^2/day) NH_4	PO_4^{3-}	H_4SiO_4
SABIN POINT				
7.12.1977	SP3.77SB	0.95	0.21	0.51
	SP4.77SB	1.1	0.22	0.91
	SP5.77SB	1.4	0.21	0.60
8.29.1977	SP7.77FB	1.1	0.07	0.36
	SP8.77SB	1.3	0.07	0.65
	SP9.77SB	0.59	0.09	0.68
	SP10.77FT	0.94	0.07	0.73
		1.1 ± .3	0.13 ± .07	0.63 ± .17
WARWICK NECK				
8.15.1977	WN1.77ST	0.20	0.04	0.41
	WN2.77ST	0.04	—	0.25
	WN3.77FT	0.28	0.02	0.51
	WN4.77FT	0.22	—	—
	WN5.77FB	0.15	—	0.18
		0.18 ± .09	0.03	0.34 ± .15
BRENTON REEF				
9.12.1977	BR5.77ST	0.17	0.01	0.67
	BR6.77FT	0.10	0.01	1.0
	BR7.77FT	0.34	0.04	1.4
	BR8.77ST	0.54	0.03	1.2
10.25.1977	BR10.77ST	—	—	—
	BR13.77FB	0.01	0.00	—
		0.23 ± .21	0.02 ± .02	1.1 ± .3

* S = static flux experiment; F = flow-through flux experiment; B = box core; T = tube core.

a further 30 minutes before commencing the flux experiments. Two types of experiments were conducted. In the "static" flux experiments samples of supernatant water were withdrawn periodically over 24 hrs using a 50 ml syringe and were replaced with equal volumes of bottom water. In the "flow through" experiments the supernatant water was continuously replaced by bottom water using a peristaltic pump, and samples of the exit water were collected periodically over 24 hrs. Flow rates (2-6 ml/min) were chosen so that the half-time for exchange of the supernatant water was about half that of the duration of the experiment.

Samples were filtered through 0.4 μm Nuclepore filters before analysis. The laboratory-incubated flux samples were analyzed for ammonia, nitrate plus nitrite, phosphate, silica, manganese, iron, copper, nickel, and cadmium; and the *in situ* flux samples were analyzed for ammonia, phosphate, silica, and manganese. The analytical techniques used are described in Elderfield and others (1981).

RESULTS

In-situ flux measurements. — The nutrient and manganese flux measurements are listed in tables 1 and 2, respectively. These compare with summer 1975 fluxes measured at the Jamestown North site of 0.27 ± 0.08 μmoles $NH_3/cm^2/day$, 0.07 ± 0.02 μmoles $PO_4^{3-}/cm^2/day$, 1.2 ± 0.2

TABLE 4

Laboratory-incubated flux measurements: manganese

Site/date/core no.*		Flux (μmoles/cm^2/day)	k_a (/min)**
SABIN POINT			
7.12.1977	SP3.77SB	0.070	2.3×10^{-3}
	SP4.77SB	0.044	1.6×10^{-3}
	SP5.77SB	0.054	1.9×10^{-3}
8.29.1977	SP7.77FB	0.022	—
	SP8.77SB	0.045	2.2×10^{-3}
	SP9.77SB	0.018	0.83×10^{-3}
	SP10.77FT	0.026	—
		0.040 ± 0.019	$1.8 (\pm 0.6) \times 10^{-3}$
WARWICK NECK			
8.15.1977	WN3.77ST	0.031	1.6×10^{-3}
	WN5.77FB	0.021	—
		0.026	1.6×10^{-3}
BRENTON REEF			
9.12.1977	BR5.77ST	0.061	1.4×10^{-3}
	BR6.77FT	0.083	—
	BR7.77FT	0.082	—
	BR8.77ST	0.087	1.7×10^{-3}
10.25.1977	BR10.77ST	0.012	0.13×10^{-3}
	BR13.77FB	0.026	—
		0.059 ± 0.032	$1.1 (\pm .8) \times 10^{-3}$

* S = static flux experiment; F = flow-through flux experiment; B = box core; T = tube core.

** k_a = first-order apparent rate constant for Mn^{2+} oxidation (see text for method of calculation). Mean and standard deviation for k_a (omitting the apparently anomalous results for SP9.77 and BR10.77) is $1.8 (\pm 0.3) \times 10^{-3}$/min.

μmoles $H_4SiO_4/cm^2/day$ (McCaffrey and others, 1980), and 0.049 ± 0.018 μmoles $Mn/cm^2/day$ (Graham, Bender, and Klinkhammer, 1976).

Laboratory flux measurements in the static mode. — Typical results for the nutrients and manganese from the "static" flux experiments are illustrated in figures 2 and 3, respectively. In the case of the nutrients, concentrations increase linearly with time, and fluxes were obtained directly from the slopes of these plots multiplied by the ratio of supernatant-water volume to core surface area (table 3).

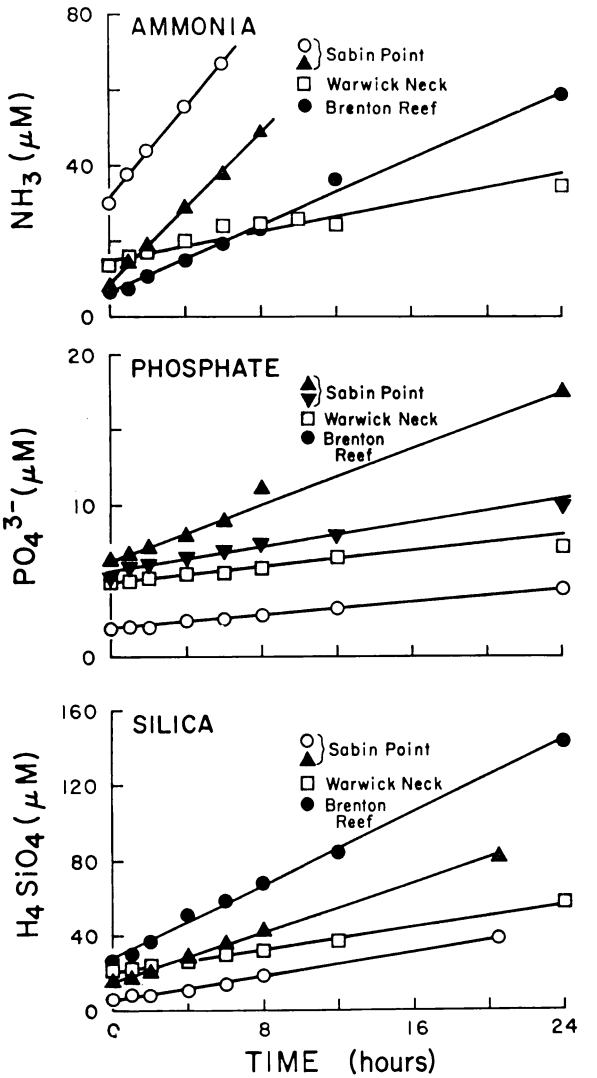

Fig. 2. Ammonia, phosphate, and silica results from laboratory-incubated "static" flux experiments. Open circles, SP4.77; upright filled triangles, SP5.77; reversed filled triangles, SP8.77; open squares, WN3.77, filled circles, BR8.77.

The concentration-time relationships for manganese show distinct curvature which we interpret to indicate the loss of Mn^{2+} from solution by oxidation. Because of the large surface area for precipitation afforded by the high particle density at the sediment-seawater interface, manganese oxidation kinetics can be regarded as first-order, and, according to Brewer and Elert (ms) the rate law for Mn^{2+} oxidation is

$$\frac{d[Mn^{2+}]}{dt} = k[Mn^{2+}]\,[MnO_2]\,[OH^-]^2\,[O_2]$$

where

$[\,]$ = concentration
t = time
k = first-order rate constant.

We assume here that $[MnO_2]$, pH, and pO_2 remain constant because of constant aeration. Thus, the relationships shown in figure 3 are described by the equation

$$\frac{d[Mn^{2+}]}{dt} = F_B \cdot \frac{A}{v} - k_a[Mn^{2+}]$$

where

F_B = the benthic flux of manganese
A/v = the ratio of the surface area of the core to the volume of supernatant water
k_a = the first-order apparent rate constant for Mn^{2+} oxidation = $k[MnO_2]\,[OH^-]^2\,[O_2]$.

In order to obtain the benthic flux from this equation two possibilities must be recognized. One is that the benthic flux may decrease throughout

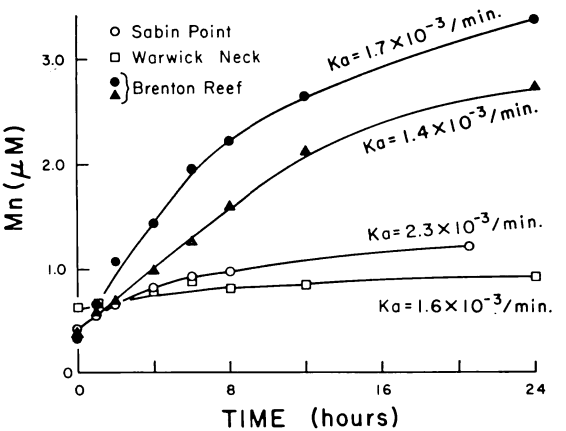

Fig. 3. Manganese results from laboratory-incubated "static" flux experiments. Open circles, SP3.77; filled triangles, BR5.77; filled circles, BR8.77; open squares, WN3.77. k_a = first-order apparent rate constant of Mn^{2+} oxidation (see text).

the duration of the experiment in response to the increasing manganese content of the supernatant solution and the consequent decrease in concentration gradient between Mn^{2+} in supernatant water and interstitial water (variable flux model). Alternatively, the benthic flux may remain constant throughout the experiment, and the curvature in the manganese versus time plot may reflect only Mn^{2+} oxidation and precipitation (constant flux model). Thus, the calculated manganese flux is model dependent but, as it transpires, only marginally so.

For the constant flux model, the solutions of the above equation are

$$F_B = \frac{v}{A} \cdot k_a[Mn^{2+}]_{ss}$$

$$\frac{[Mn^{2+}]_{ss} - [Mn^{2+}]}{[Mn^{2+}]_{ss} - [Mn^{2+}]_o} = \exp(-k_a t)$$

where

$[Mn^{2+}]_{ss}$ = the steady-state manganese concentration
$[Mn^{2+}]_o$ = the manganese concentration at $t = 0$.

Using an iterative procedure the experimental results were fitted to an exponential of the form shown above and gave the flux values and apparent rate constants listed in table 4. The correlation coefficients we obtained were extremely good, $r > 0.997$ for all cores except two (SP9.77 and BR10.77) where $r = 0.983$, and in these two cases the calculated k_a values were somewhat lower than for the remainder. With these exceptions, values of k_a were very similar for all experiments.

For the variable flux model, the equation describing the concentration-time relationship becomes

$$\frac{d[Mn^{2+}]}{dt} = D \frac{d[Mn^{2+}]}{dz} \cdot \frac{A}{v} - k_a[Mn^{2+}]$$

where

D = ionic diffusion coefficient of manganese in the interstitial water
$\frac{d[Mn^{2+}]}{dz}$ = concentration gradient of manganese between interstitial water and supernatant water.

Assuming that the manganese concentration gradient in the top centimeter of the core is constrained by the pore water $[Mn^{2+}]$ at 1 cm depth (called here $[Mn^{2+}]_{IW}$) which is constant, then

$$\frac{d[Mn^{2+}]}{dt} = D \cdot \frac{A}{v} \cdot \frac{[Mn^{2+}]_{IW} - [Mn^{2+}]}{z} - k_a[Mn^{2+}]$$

where $z = 1$ cm. This equation has a solution

$$\frac{[Mn^{2+}]_{ss} - [Mn^{2+}]}{[Mn^{2+}]_{ss} - [Mn^{2+}]_o} = \exp\left(-\frac{DA}{zv} t\right) \exp(-k_a t)$$

where

$$[Mn^{2+}]_{ss} = \frac{DA}{zv}\ [Mn^{2+}]_{IW} / \left(\frac{DA}{zv} + k_a\right)$$

Using $D_{Mn^{2+}} = 0.3 \times 10^{-5} cm^2/sec$ (McCaffrey and others, 1980), values of the term DA/zv range between 9.7×10^{-6}/min and 1.8×10^{-5}/min for the various experiments, about two orders of magnitude lower than values of k_a (table 4). Thus, the assumption of a constant benthic flux is reasonable. Figure 4B compares values of exp (–DA/zv t) and exp ($-k_a t$) and shows that invoking this assumption does not lead us to overestimate the flux by more than 2.5 percent.

Laboratory flux measurements in the flow-through mode. — Typical results for the nutrients and manganese from the "flow-through" experiments are illustrated in figure 5. The concentration versus time relationships for these experiments (using the constant flux model) are described (for example, for manganese) by the equation

$$\frac{d[Mn^{2+}]}{dt} = F_B \cdot \frac{A}{v} - k_a[Mn^{2+}] + \frac{F_W}{v}([Mn^{2+}]_{IN} - [Mn^{2+}])$$

where

F_W = the flux of input water
$[\,]_{IN}$ = concentration in the input water

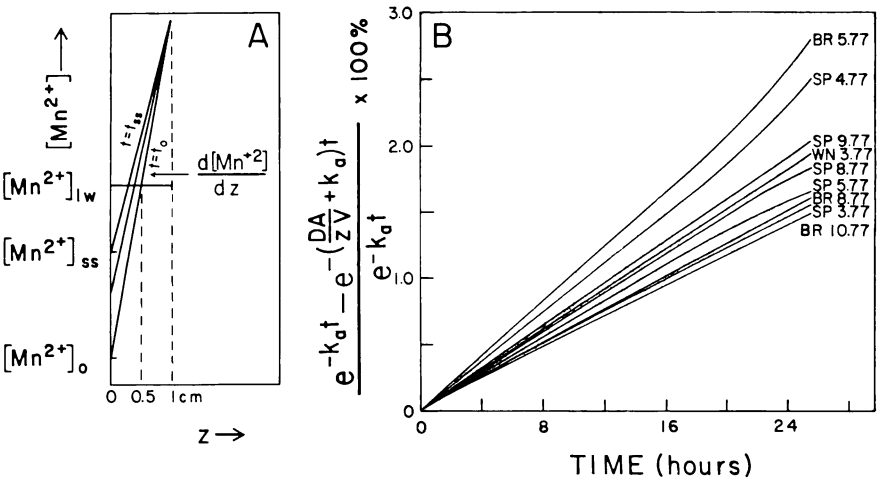

Fig. 4. (A) Schematic illustration to show the assumed effect of the increasing Mn^{2+} concentrations in supernatant water, $[Mn^{2+}]$, on $d[Mn^{2+}]/dz$, the concentration gradient of Mn^{2+} in the interstitial water of the underlying sediment. The gradients are constrained by $[Mn^{2+}]_{IW}$, the interstitial Mn^{2+} concentration in the 0 to 1 cm section of the sediment, and decrease in $d[Mn^{2+}]/dz$ as the supernatant Mn^{2+} concentration increases from its initial value, $[Mn^{2+}]_o$, to its steady-state value, $[Mn^{2+}]_{ss}$.

(B) Comparison of the exponential term in the variable flux model $\left(\exp\left(-\frac{DA}{zV} + k_a\right)t\right)$ with the exponential term in the constant flux model ($\exp -k_a t$) for manganese (see text) where the process shown in figure 4A is considered. The plots show the percent difference between these terms as a function of time for the 9 cores used in the "static" flux experiments.

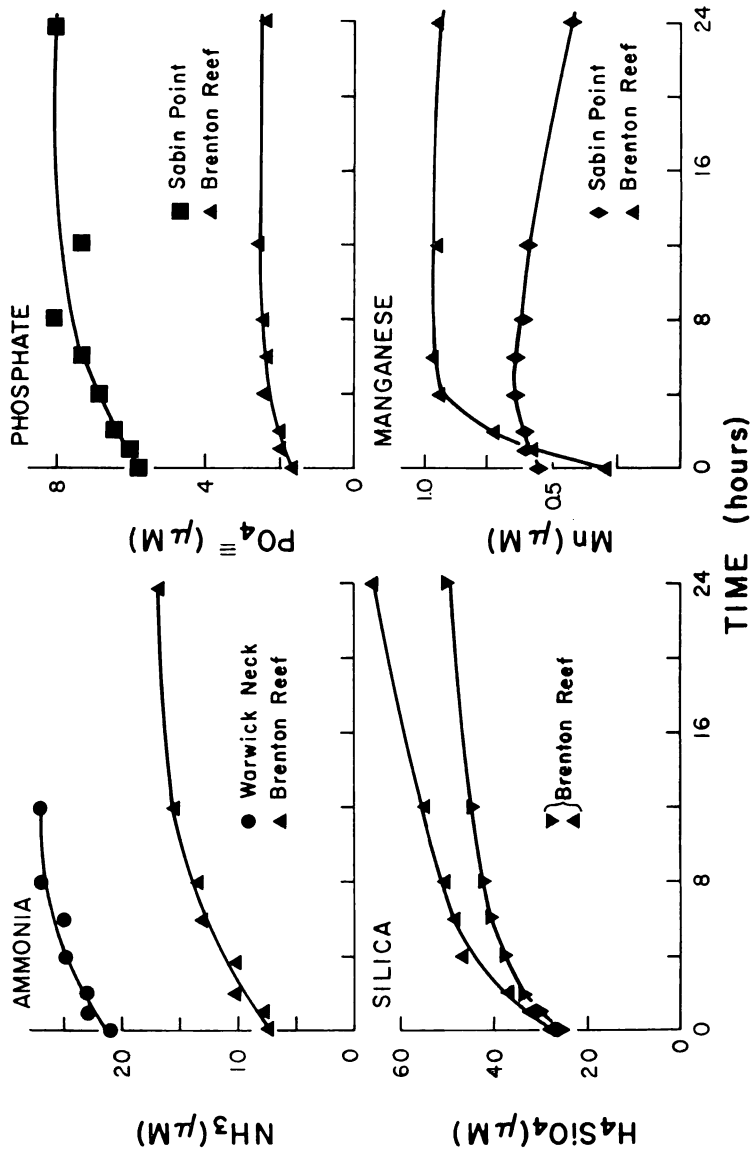

Fig. 5. Nutrient and manganese results from laboratory-incubated "flow-through" experiments. Circles, WN5.77; upright triangles, BR7.77; squares, SP10.77; reversed triangles, BR6.77; lozenges, SP7.77.

Assuming a constant benthic flux, the solutions are

$$F_B = \frac{V}{A} \cdot k_a[Mn^{2+}]_{ss} + \frac{F_W}{A}([Mn^{2+}]_{ss} - [Mn^{2+}]_{IN})$$

$$\frac{[Mn^{2+}]_{ss} - [Mn^{2+}]}{[Mn^{2+}]_{ss} - [Mn^{2+}]_o} = \exp\left[- \left(\frac{F_W}{v} + k_a\right) t \right]$$

Equations of this form were solved for the nutrients (with $k_a = 0$) and for manganese (with the mean value from table 4 of $k_a = 1.8 \times 10^{-3}$/min) and gave the results listed in tables 3 and 4.

Trace-element fluxes. — Analyses for nickel, cadmium, and copper were made only on samples from laboratory flux measurements in the static mode. Typical results are illustrated in figure 6. In none of the experiments was there any systematic evidence for a positive flux of Ni, Cd, or Cu out of the sediments. With only a few exceptions (which are believed to reflect contamination) all changes in nickel and cadmium concentrations were within the analytical precision (± 10 percent). This result allows us to put limits on the fluxes, and these are $0 \pm 2 \times 10^{-4}$ μmoles/cm^2/day for nickel and $0 \pm 4 \times 10^{-6}$ μmoles/cm^2/day for cadmium. Over the experimental periods as a whole, the copper results either showed no flux or showed a negative flux, that is, a flux into the sediment. This was particularly apparent at the Sabin Point site, and the magnitude of this flux was approx -4×10^{-4} μmoles/cm^2/day. The copper results from the Sabin Point site show a curious feature, the high concentrations observed in the water at the start of each experiment. We do not understand the significance of this result. One possibility is that these initial samples are contaminated. If real, the high Cu values might reflect oxidation of Cu-rich sedimentary sulphides at the time the supernatant water is changed or release of copper from decomposing organic tissue and a kinetic lag in scavenging by sedimentary sulphides.

DISCUSSION

Results of benthic flux determinations for the nutrients and manganese are summarized in figures 7 and 8, respectively. These summaries include the Jamestown North summer 1975 flux data of McCaffrey and others (1980) for nutrients and of Graham, Bender, and Kinkhammer (1976) for manganese. Three conclusions emerge from these data. First, fluxes obtained by different measurement techniques are similar for comparable samples. Second, within the scatter of the data from any one season (about a factor of three if we omit a few anomalously high flux values), manganese and silica fluxes are similar at all study sites, but fluxes of ammonia and phosphate show significant spatial variation, with relatively high values in the upper bay (Sabin Point) and relatively low values in the lower bay (Jamestown North) and Rhode Island Sound (Brenton Reef). Third, there is a seasonal trend, with fluxes being higher in the summertime and lower in the wintertime.

Spatial variation in fluxes. — This spatial variability in the fluxes of nutrients directly reflects differences in interstitial-water chemistry between sites. As shown by Elderfield and others (1981), gradients of TCO_2, sulphate, ammonia, and phosphate versus depth are steeper at the SP site than at the JN and BR sites, and the RN profiles are intermediate between these extremes. For example, ammonia concentrations in interstitial waters at a depth of 0 to 1 cm are 500 μM at the SP site but 100 μM at the JN site. Differences of this sort will promote higher diffusive fluxes of ammonia and phosphate in the upper bay. For silica, on the other

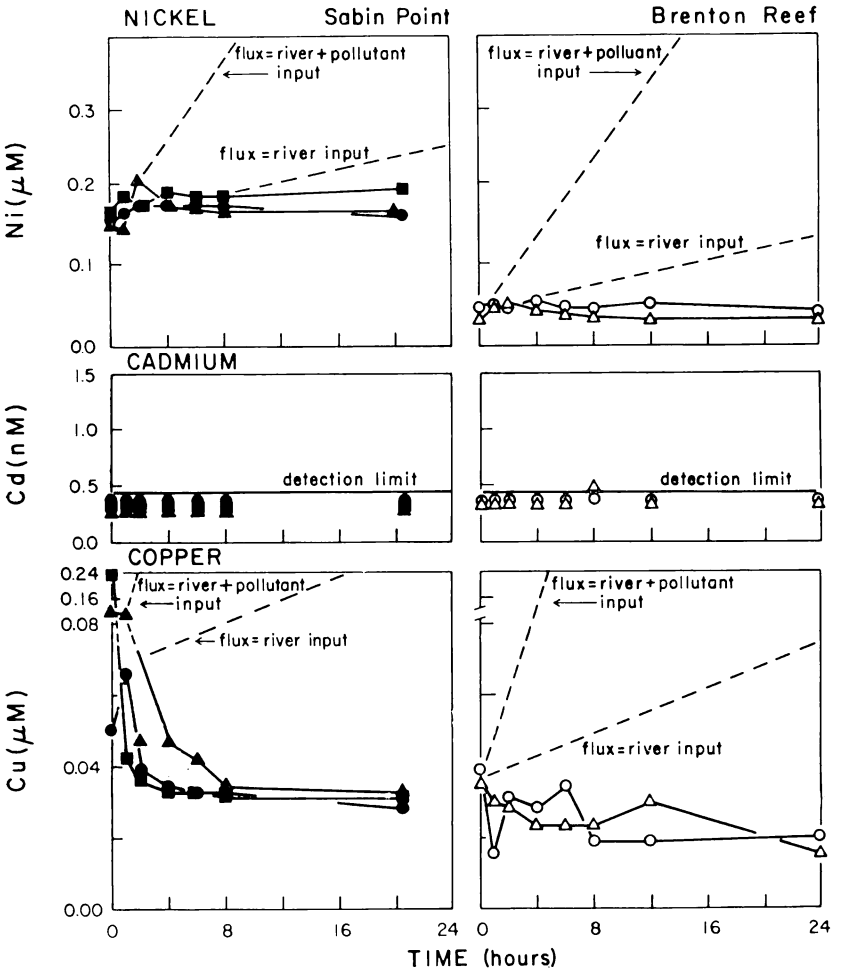

Fig. 6. Nickel, cadmium, and copper results from laboratory-incubated "static" flux experiments. Filled circles, SP3.77; filled squares, SP4.77; filled triangles, SP5.77; open circles, BR5.77; open triangles, BR8.77. The dashed lines show the trace metal concentration increases giving fluxes equal to river input to Narragansett Bay (using data from Bender and the Narragansett Bay Study Group, 1978) and increases equivalent to river plus pollutant input.

hand, our studies showed that core-top interstitial concentrations are similar at all stations, and the broad similarity in benthic fluxes reflects this.

Bioturbation affects interstitial water profiles but is only a moderate influence on the relation between benthic fluxes and core-top interstitial concentrations. Differences do exist in interstitial-water silica profiles, for example, over the 5 to 20 cm depth range (see for example, fig. 3 of Elderfield and others, 1981) simply because the sediment at the JN and BR sites is bioturbated, whereas the sediment at the SP and RN sites is apparently far less disturbed. However, bioturbation is unlikely to affect the benthic flux significantly since, as McCaffrey and others (1980) have shown for the bioturbated JN site, diffusion transports ammonia faster than the pumping activities of the macrobenthos and transports phosphate and silica at about the same rate. Most of the nutrient release to

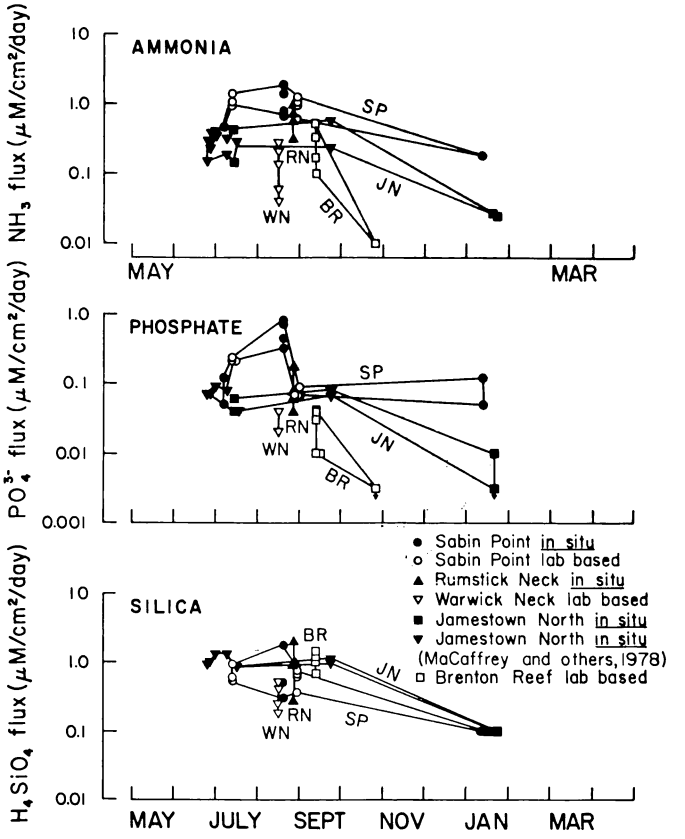

Fig. 7. Summaries of benthic flux results for ammonia, phosphate, and silica shown as a function of measurement data. Flux units are abbreviated and are μmoles/cm²/day.

interstitial waters occurs within the upper 1 cm of the sediment; consequently the loss by diffusion is extremely rapid.

The ratios of the average fluxes at each site are listed in table 5. The ammonia to phosphate ratio of between 3 and 12 implies that the N/P ratio of decomposing material within the sediment is somewhat lower than the value normally attributed to marine phytoplankton and similar tissue. This agrees with the observations of Hale (ms) and is also in agreement with our interstitial-water studies which showed phosphate profiles atypical for marine organic matter and suggestive of a contribution from an inorganic phosphrous source (Elderfield and others, 1981). Alternatively, Hale (ms) suggested that the anomalous element was not P, which he regarded as being solely metabolic, but N, which, he argued, was low due to N consumption.

Temporal variation in fluxes. — One of the clearest generalizations that may be made from figures 7 and 8 is that of the seasonal pattern in benthic fluxes. Of the nutrients, the seasonal contrast is most clearly seen for silica, where winter fluxes are barely measurable (0.1 μmoles/cm^2/day) whereas summer fluxes average ~1 μmole/cm^2/day, an order of magnitude higher. Perhaps the greatest seasonal contrast is evident for manganese (fig. 8). As a background to figure 8 we have displayed the seasonal variation in temperature of bottom waters in Narragansett Bay (based upon 1972-1973 data which are summarized in Kremer and Nixon, 1978)

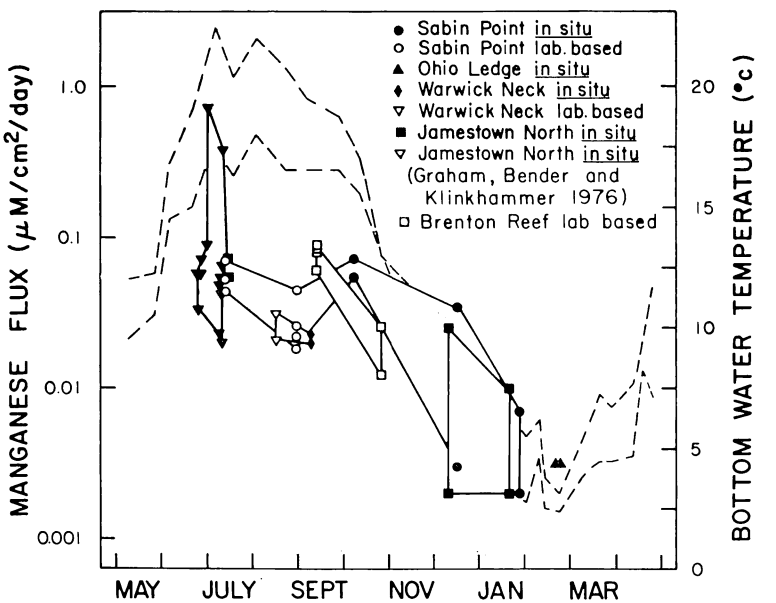

Fig. 8. Summary of benthic flux results for manganese shown as a function of measurement date. The dashed lines (data from Kremer and Nixon, 1978) show the range and seasonal variation in bottom-water temperature of Narragansett Bay. Flux units are abbreviated and are μmoles/cm^2/day.

to show that warm-water (~20°C) fluxes are an order of magnitude or more higher than cold-water (~5°C) fluxes.

Hale (ms) and Nixon, Oviatt and Hale (1976) found a similar seasonal variation in fluxes at 3 sites in the center of the Bay. The summer flux maximum follows the Winter-Spring phytoplankton bloom and may merely reflect the food supply to the benthos. On the other hand, the seasonal cycle could reflect the temperature dependence of metabolic activity. Table 6 summarizes the measured summer and winter fluxes for the Sabin Point and Jamestown North sites together with estimates of "apparent activation energies" (Vosjan, 1974; Goldhaber and others, 1977; Aller, ms), a theoretically-uncertain but analytically useful device for linking the fluxes to summer and winter temperatures and describing their sensitivity to temperature change. The differences between measured summer and winter metabolite fluxes imply activation energies which are similar to those obtained by Aller (ms). As discussed by Aller (ms) these coefficients of temperature dependence are similar to values for sulphate reduction and to energies of enzymatic reactions. The literature value for silica shown for comparison with measured values may not be completely appropriate, since this is for amorphous silica dissolution whereas interstitial silica concentrations probably reflect silica input by diatom dissolution and also reaction with clay minerals.

Comparison of measured and calculated fluxes. — In addition to summarizing the measured flux data, table 6 also lists benthic fluxes calculated from our interstitial-water data (Elderfield and others, 1981) using the procedures of McCaffrey and others (1980), and assuming that there is negligible advective water flux for Jamestown North in the winter-time and for Sabin Point at all times.

Narragansett Bay interstitial-water studies of McCaffrey and others (1980) and Elderfield and others (1981) showed that the interstitial-water

TABLE 5

Benthic-flux ratios

Site/experiment*	$\frac{NH_3}{PO_4^{3-}}$	$\frac{NH_3}{H_4SiO_4}$
SABIN POINT		
1.	8.5	1.8
2.	2.9	1.7
RUMSTICK NECK		
2.	7.2	0.69
WARWICK NECK		
1.	6.0	0.53
JAMESTOWN NORTH		
2.	5.3	—
3.	3.9	0.23
BRENTON REEF		
1.	11.5	0.21

* 1. = laboratory-incubated flux experiments; 2. = *in-situ* flux experiments; 3. = from data of McCaffrey and others (1980).

profiles reflect, in part, a balance between metabolic rates and rates of bioturbation. At the Sabin Point site the high rate of diagenesis or low rate of bioturbation produces profiles typically diffusion controlled, whereas at the Jamestown North site the effect of bioturbation is dominant. McCaffrey and others (1980) have shown that diffusion and bio-advection are equally important in the transport of nutrients and manganese at the JN site. They have also shown that the sum of the calculated fluxes attributable to these processes approximates their measured (summer) fluxes at this site, and their calculated fluxes are included in table 6. Although we have not measured the "biopumping" rate of organisms at the Sabin Point site, we have made X-radiographs of the sediment, and these show that there is a very sparse infaunal community with little or no evidence of the burrows and tubes indicative of the circulation of seawater and intersitial water by animals. Thus, the advection rate should be far less at Sabin Point than at Jamestown North. The results in table 6 are compatible with this observation. A comparison of the calculated diffusive fluxes and the measured summer fluxes shows that diffusion alone can account for all of the measured nutrient fluxes at Sabin Point, whereas it cannot account for the measured fluxes at Jamestown North.

Within the uncertainties of the flux measurements and the variations in interstitial-water concentration gradients for each site, the calculated nutrient fluxes for both summer and winter agree with the measured fluxes, except for the winter ammonia fluxes where the calculated value is somewhat higher than that measured. This suggests that the system is reasonably-well characterized. For manganese, however, the measured summer flux at Sabin Point is much higher than the calculated flux. The low calculated summer manganese flux may reflect a drastic error in our assumption about the shape of the manganese concentration gradient in the interstitial waters. We assumed that $[Mn^{2+}]$ increases linearly with depth in the top centimeter as illustrated in figure 4A. Below 1 cm depth, measured interstitial manganese concentrations decrease. This observation suggests that the true shape of the $[Mn^{2+}]$ profile at the core top may involve a dramatic increase to a maximum in the top few millimeters and a decrease below. In either case the absolute $[Mn^{2+}]$ values are constrained by the interstitial-water $[Mn^{2+}]$ in the 0 to 1 cm interval, but if the second case is correct, $d[Mn^{2+}]/dz$ at the interface must be far higher than we assumed for the table 6 calculations, and the diffusive Mn^{2+} flux would be correspondingly greater.

Trace-element fluxes. — Benthic fluxes of nickel, cadmium, and copper are close to zero or are negative (fig. 6). This result is compatible with our interstitial-water studies (Elderfield and others, 1981) which, in general, show that trace metal concentrations decrease rapidly with depth and become undetectable within a few cm of the sediment-seawater interface. We have attributed this behavior to scavenging by sulphides, and this suggests that there is a small net flux of sulphide-forming metals (Cu, Cd, Zn, Ni, Pb . . .) into anoxic sediments rather than a flux out. Our results are in agreement with the *in-situ* study of Bender, McCaffrey, and

TABLE 6
Summary of flux calculation

chemical and site	summer: measured flux (μM/cm^2/day)	summer: calculated flux (μM/cm^2/day)*: diffusive flux: dC/dz (μM/cm^4)	summer: calculated flux (μM/cm^2/day)*: diffusive flux: D** (10^5 cm^2/sec)	summer: calculated flux (μM/cm^2/day)*: diffusive flux: flux	summer: calculated flux (μM/cm^2/day)*: advective flux	summer: calculated flux (μM/cm^2/day)*: total flux
AMMONIA						
Sabin Point	1.2 ±.5[a] 0.46[a] 1.1 ±.3[b] 0.92	1.03 ±.40	0.89	0.79±.31	0	0.79
Jamestown North	0.27[c] 0.29[a] 0.28	—		0.17	0.07	0.24
PHOSPHATE						
Sabin Point	0.56±.22[a] 0.09[a] 0.13±.07[b] 0.26	0.69 ±.35	0.33	0.20±.10	0	0.20
Jamestown North	0.05[a] 0.07[c] 0.06	—		0.016	0.02	0.036
SILICA						
Sabin Point	0.83[a] 0.63±.17[b] 0.73	0.98 ±.36	0.45	0.38±.14	0	0.38
Jamestown North	1.2[c]	—		0.27	0.3	0.57
MANGANESE						
Sabin Point	0.064[a] 0.040±.019[b] 0.052	0.007±.0014	0.31	0.002±.0004	0	0.002
Jamestown North	0.064[a] 0.049[c] 0.057	—		0.02	0.01	0.03

* Jamestown North data except for Si winter flux calculations from McCaffrey and others (1980) with diffusion fluxes corrected to 20°C (summer) and 5°C (winter).

** Diffusion coefficients are assumed to be 50 percent of the values in deionized water given by Li and Gregory (1974) corrected to summer and winter temperatures.

Cullen (ms) who determined fluxes of -2.6 (± 3.8) $\times 10^{-5}$ μmoles/cm^2/day for cadmium, -1.4 (± 6.9) $\times 10^{-4}$ μmoles/cm^2/day for copper and -6.0 (± 10.9) $\times 10^{-4}$ μmoles/cm^2/day for nickel.

The only situation where the agreement between the flux measurements and the interstitial-water results is equivocal is for the behavior of copper at the Sabin Point site. Interstitial-water profiles show, in some instances (Elderfield and others, 1981, fig. 23), that copper concentrations within the upper 1 cm are higher than in local bottom waters (but then decrease rapidly to undetectable values), and this implies that there is a diffusive flux of copper out of the sediment. The copper enrichment in interstitial waters at 0 to 1 cm from the Sabin Point site is 0.15×10^{-3} μmoles/cm^3, and this predicts a diffusive flux (using $D_{Cu^{2+}} = D_{Mn^{2+}}$, see table 6) of $+4 \times 10^{-5}$ μmoles/cm^2/day. The sign of this predicted flux is the opposite of that measured in our flux experiments, and we are at a loss to explain the discrepancy. On the other hand, the predicted flux is

for nutrients and manganese§

winter						
	calculated flux (μM/cm^2/day)*					"apparent activation energy", E and literature values of E
	diffusive flux					
measured flux (μM/cm^2/day)	dC/dz (μM/cm^4)	D** (10^5 cm^2/sec)	flux	advective flux	total flux	(kcal/mole)
0.18[a]	1.03 ±.40	0.59	0.53 ±.21	0	0.53	20
0.028[a]	—		0.11	0	0.11	25 16-26[1.] (18-25)[2.]
0.09[a]	0.69 ±.35	0.22	0.13 ±.07	0	0.13	12
0.01[a]	—		0.011	0	0.011	19 (18-25)[2.]
0.1[a]	0.34 ±.13	0.30	0.087±.032	0	0.087	20
0.1[a]	0.20		0.053	0	0.053	27 20[3.]
0.004[a]†	0.007±.0014	0.21	0.001±.0002	0	0.001	28
0.005[a]†	—		0.013	0	0.013	26 28-57[1.]

† One outlying result is excluded (see table 2). [a] *in situ* flux measurements; [b] laboratory-incubated flux measurements; [c] published data (Graham, Bender, and Klinkhammer, 1976; McCaffrey and others, 1980). [1.] Aller (ms); [2.] Vosjan (1974), Goldhaber and others (1977), Aller (ms); [3.] Wollast (1974).

§ Flux units are abbreviated and are μmoles/cm^2/day. Concentration gradient units are abbreviated and are μmoles/cm^4.

very small and would be negligible in terms of the Cu mass balance of the Bay.

A nutrient and metal balance for Narragansett Bay. — A useful way of placing benthic fluxes in a realistic context is to demonstrate their significance in geochemical budgets of the Bay. Hale (ms) performed this exercise and demonstrated the importance of benthic fluxes in the Bay nutrient balance. We repeat the calculations here. In table 7 we show the benthic fluxes within the context of a nutrient and metal balance for Narragansett Bay made in the Spring of 1977 by Bender and the Narragansett Bay Study Group (ms). The benthic fluxes measured at Sabin Point were assumed to be typical of the upper bay (taken as 25 percent of the total area), and those at Jamestown North were assumed to be typical of the remainder of the bay; and the data were adjusted to March-

TABLE 7

Benthic fluxes, riverine fluxes, and doubling times for nutrients and metals in Narragansett Bay

	flux (moles/sec)		Amount present (moles)	Doubling time (days)
	river input*	benthic fllux to Bay water		
NH_3	4.5	+2.3	1×10^6	5
PO_4^{3-}	0.98	+0.99	0.7×10^6	8
H_4SiO_4	19	+3.6	4×10^6	13
Mn	0.40	+0.17	0.7×10^6	48
Ni	0.031	−0.018	0.2×10^6	—
Cd	—	−0.0008	—	—
Cu	0.013	−0.004	0.1×10^6	—

*Data from Bender and the Narragansett Bay Study Group (ms) includes pollutant inputs of nutrients and, for PO_4^{3-} and H_4SiO_4, import fluxes by Block Island Sound water. Pollutant inputs of Ni and Cu estimated at 0.029-0.27 moles/sec and 0.019-0.016 moles/sec, respectively.

April 1977 temperatures using the "apparent activation energies" listed in table 6.

The results show that benthic fluxes of ammonia, phosphate, silica, and manganese are important sources. The sediment may be an important sink for trace metals, but the large uncertainties in the benthic flux data (and in the estimates of pollutant inputs) make this conclusion highly equivocal. Table 7 also lists "doubling times" obtained by dividing the amount of each element present in the Bay water by its benthic flux. Comparison of these values with the flushing time for the bay, which is 2 to 4 weeks, further demonstrates the importance of benthic fluxes in the geochemical balance of the bay.

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REFERENCES

Aller, R. C., ms, 1977, The influence of macrobenthos on chemical diagenesis of marine sediments: Ph.D. thesis, Yale Univ., 600 p.

Bender, M. L., McCaffrey, R. J., and Cullen, J. D., 1978, The release of heavy metals from reducing marine sediments, *in* Jacoff, Francine, ed., Advances in Marine Research, Proceedings of a symposium on the state of Marine Environmental Research: U.S. Environmental Protective Agency, Environmental Research Laboratory, Narragansett.

Brewer, P. G. and Elert, M., ms, 1972, The kinetics of manganese oxidation in seawater: unpub. manuscript.

Elderfield, H., McCaffrey, R. J., Luedtke, N., Bender, M., and Truesdale, V. W., 1981, Chemical diagenesis in Narragansett Bay sediments: Am. Jour. Sci., v. 281, in press.

Goldhaber, M. B., Aller, R. C., Cochran, J. K., Rosenfeld, J. K., Martens, C. S., and Berner, R. A., 1977, Sulfate reduction, diffusion, and bioturbation in Long Island Sound sediments: report of the FOAM group: Am. Jour. Sci., v. 277, p. 193-237.

Graham, W. F., Bender, M. L., and Klinkhammer, G. P., 1976, Manganese in Narragansett Bay: Limnology Oceanography, v. 21, p. 665-673.
Hale, S., ms, 1974, The role of benthic communities in the nutrient cycles of Narragansett Bay: M.S. thesis, Univ. Rhode Island, 129 p.
Kremer, J., and Nixon, W. S., 1978, A coastal marine ecosystem, *in* Ecological studies, no. 24: Bonn, Springer Verlag, p.
McCaffrey, R. J., Myers, A. C., Davey, E., Morrison, G., Bender, M., Luedtke, N., Cullen, D., Froelich, P., and Klinkhammer G., 1980, Benthic fluxes of nutrients and manganese in Narragansett Bay, Rhode Island: Limnology Oceanography, v. 25, p. 31-44.
Nixon, W. S., Oviatt, C. A., and Hale, S. S., 1976, Nitrogen regeneration and the metabolism of coastal marine bottom communities, *in* Anderson, J. M., and A. Macfayden, eds., The role of terrestrial and aquatic organisms in decomposition processes: Oxford, Blackwell Sci. Pub. p. 269-283.
Vosjan, J. H., 1974, Sulfate in water and sediment of the Dutch Wadden Sea: Netherlands Jour. Sea Research, v. 8, p. 208-213.
Wollast, R., 1974, The silica problem, *in* Goldberg, E. D., ed., The Sea, v. 5, Marine Chemistry: New York, Wiley-Intersci., p. 359-392.