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Sediment-water exchange in shallow water estuarine sediments

by Steven Emerson,¹ Richard Jahnke^{1,2} and David Heggie³

ABSTRACT

Pore water profiles in shallow estuarine sediments of Puget Sound show the characteristics of enhanced interstitial-water transport by animal activity. Using an *in situ* ³H experiment and dissolved silicate profiles we evaluate the transport parameter due to animal activity in the surface 20 cm of sediments to be $1-5 \times 10^{-7} \text{ s}^{-1}$ which is in the range of similar parameters determined in other nearshore environments in the U.S. The fluxes of alkalinity, ammonia and silicate across the sediment-water interface due to biological processes are greater than that by one-dimensional molecular diffusion. For the metals Fe, Mn, Cu, Ni and Cd the dominant transport mechanism depends upon the depth at which the metal is released to the pore waters. Probably the most important effect of biological activity on metal remobilization is the removal of sulfide from the pore waters, via ventilation of sediments with oxic overlying water, allowing the enrichment of dissolved metals which might otherwise be very low in concentration due to insoluble sulfide formation. The result is a greatly enhanced flux of metals to the bottom waters.

1. Introduction

Most reactive inorganic and organic pollutants that are introduced to the environment will, at some point in their journey to the sea, be buried or recycled within estuaries. Processes at the estuarine sediment-water interface play an important role in determining the ultimate fate of these substances. In this paper we describe an investigation of the chemical and physical processes that occur near the sediment-water interface in Puget Sound and the influence of these processes on the metal and nutrient behavior in the sediments.

Previous investigations of sediment-water exchange mechanisms and rates in the nearshore environments of Long Island Sound (Goldhaber *et al.*, 1977; Aller, 1980a, b), Narragansett Bay (Luedtke and Bender, 1979; McCaffrey *et al.*, 1980), Cape Lookout Bight, North Carolina (Kipphut and Martins, 1982), the Hudson River

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Estuary (Hammond *et al.*, 1977), San Francisco Bay (Hammond and Fuller, 1979; Korosec, 1979), the North Sea (Vanderborgh *et al.*, 1977) the Washington continental shelf (Smethie *et al.*, 1981; Christensen *et al.*, 1984) and Puget Sound (Grundmanis and Murray, 1977) describe pore water profiles, laboratory tracer experiments, and models used to interpret their findings. In all cases, mechanisms other than sedimentation and molecular diffusion were required to explain chemical or isotope distributions in the sediments and pore waters. Benthic animal feeding and respiratory activities are important processes at the sediment-water interface in all oxic aquatic environments; however, only in the nearshore, high-energy, environments is there clear evidence that the processes are rapid enough to influence transport within the sediment pore waters as well. Since animal respiratory activities (and sometimes physical action of tides and waves) aid in the ventilation of the sediments in estuarine environments, there is no reason to assume uniformity from location to location. Precisely for this reason, one would like to attain sufficient information from different localities to determine the feasibility of generalizing about the exchange mechanisms so that meaningful predictions for pollutant behavior can be made.

In this study we describe pore water distributions in Quartermaster Harbor, Puget Sound over the period of 1976–1979 and an *in situ* tracer (tritium, ^3H) experiment designed to monitor the transport of water across the sediment-water interface. Transport mechanisms are evaluated using a one-dimensional model with a “non local” (Imboden, 1981) source/sink term to describe the distribution of ^3H and silicate. This value is used to assess the influence of the transport processes on the fluxes of alkalinity, ammonia, silicate, and the metals, iron manganese, copper, nickel, and cadmium across the sediment-water interface. Finally, we compare the magnitude of the effect of animal activity on sediment-water exchange in Quartermaster Harbor with results from other work in estuaries and nearshore environments.

2. Methods

a. Pore water sampling. Quartermaster Harbor is a relatively shallow embayment in Puget Sound north of Tacoma, Washington. It was chosen as the sampling station because it is a location in Puget Sound with a mud bottom that is shallow enough to be reached easily by divers. The sample location is roughly 15 m deep and has a sediment accumulation rate of approximately 0.3 cm/yr (Carpenter *et al.*, 1978). The bottom waters are well flushed and remain oxic year round. The temperature of the water overlying the sediments is $\sim 12^\circ\text{C}$ in summer and $\sim 8^\circ\text{C}$ in the winter months. The sediment surface is flocculent with porosities on the order of 90%.

Pore waters were extracted from the sediments by three different methods. Short cores were recovered by divers in 7 cm diameter fiberglass core tubes with a series of 2 to 3 cm diameter holes in the barrel which were covered with vinyl plastic electrician's tape. Sediment from each interval was removed from the core, packed into screw cap

plastic centrifuge tubes and centrifuged at 11,000 rpm for five minutes. Supernate water was removed from the centrifuge tube and filtered through 0.4 micron polycarbonate Nucleopore filters. The procedures of sectioning the sediment into centrifuge tubes, removal of the supernate water, and filtering were originally done inside a nitrogen-filled glove bag to avoid air oxidation of reduced species dissolved in the water. After much experience we found that with our methods and very rapid handling we could also avoid oxidation even if the procedure was done in the air. During the 1978 sampling, a gravity core was sampled, providing greater depth penetration but sacrificing the sediment-water interface.

The second pore water sampling method utilized a peeper (Hesslein, 1976). The sampler is a polycarbonate spear with 1-cm deep ports at intervals of 1 cm. Before the peeper was inserted into the sediment by divers, the ports were filled with either distilled water or filtered surface seawater and covered with a sheet of 0.4 micron Nucleopore or Gelman aceto-nitril polypropylene filter paper and a filter guard. The sample was purged of oxygen by placing it in a seawater-filled PVC pipe and bubbling with nitrogen for 6–12 hours. Prepared samplers were inserted into the sediment and allowed to remain in place for two to four weeks, which should have allowed greater than 95% equilibration. After retrieval, water was removed from the samples by piercing the filter paper with a needle, removing the samples into syringes and filtering them.

The final pore water sampling method was a harpoon. A description of an instrument similar to the one we used is presented in Sayles *et al.* (1976), and further elaboration is unnecessary, except to note that a circular, screened frame, four feet in diameter, was attached to the trip plate to prevent extensive over-penetration in these soft sediments. In January 1977, all three methods were utilized at the closest possible proximity in an intercalibration. The harpoon was lowered first and then divers took cores on either side of the harpoon base plate and inserted a peeper.

The nutrients Si(OH)_4 , NH_4^+ , and PO_4^{3-} were determined colorimetrically on a spectrophotometer using the standard methods. Chloride was measured by silver nitrate titration, sulfide according to Cline's method (Cline, 1969) and alkalinity by Gran titration. Iron and manganese were analyzed by the colorimetric methods utilizing ferrozine (Stookey, 1970) and formaldoxime (Brewer and Spencer, 1971), respectively. Detection limits for Fe and Mn analyses were about 0.5 μM . Copper, nickel, and cadmium were measured by cobalt APDC coprecipitation and extraction followed by flameless atomic absorption spectrophotometry. Procedural blanks were 15, 4, and 2 nM for Cu, Ni, and Cd; the overall precision was $\pm 10\%$.

b. The tracer experiment. The rate of tritium penetration into the sediment was measured by covering 0.12 m² of sediments with a bell jar, injecting a spike of tritiated water and then coring the sediment after a predetermined period. The bell jars used

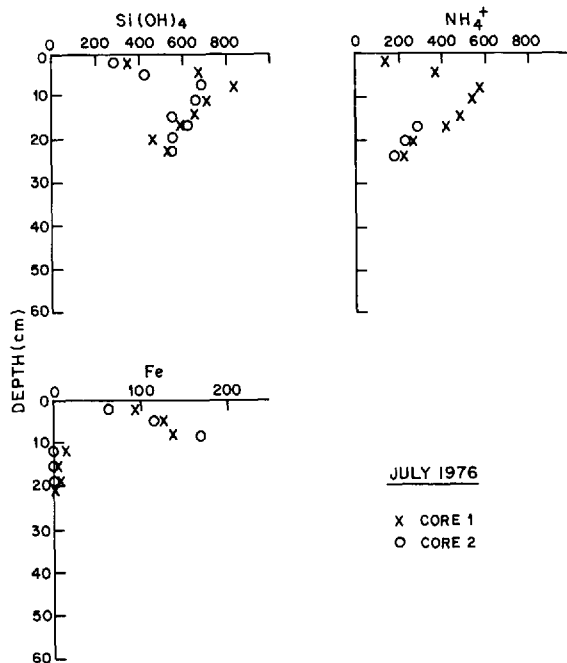


Figure 1. Pore water profiles of silicate, ammonia, and iron from sediment cores sampled by sediment squeezing in Quartermaster Harbor in July, 1976. Concentrations are $\mu\text{m/l}$.

were those described by Carpenter *et al.* (1978). They were constructed out of the top third of a 30-l polyethylene bottle and attached to a plexiglass base to increase stability on the bottom. The volume of the water enclosed was about 10 l. The bell jars were deployed by divers and secured by attaching 10 pounds of weight to the top of the base plate. The enclosed water was spiked to roughly 50,000 tritium units (TU) by injection of a 25-ml solution through a septum. The water inside the bell jar was stirred at the beginning of the experiment but not subsequently. Three separate experiments were terminated after 17, 21, and 26 hours by removing the top cap of the bell jar, inserting a 7 cm diameter core into the underlying sediment, and then removing the bell jar and retrieving the sediment core. The cores were centrifuged at 3-cm intervals as before, and tritium was counted by liquid scintillation.

3. Results

a. Pore waters. Pore water data for cruises from July 1976 through January 1979 are presented in Figures 1 through 4. In 1976 (Fig. 1) we observed the first indication of pore water distributions which have become characteristic indicators of benthic animal activity (Elderfield *et al.*, 1981; Aller, 1980b; Korosec, 1979; Grundmanis and Murray, 1977); i.e., the increase of silicate, ammonia and alkalinity to a subsurface

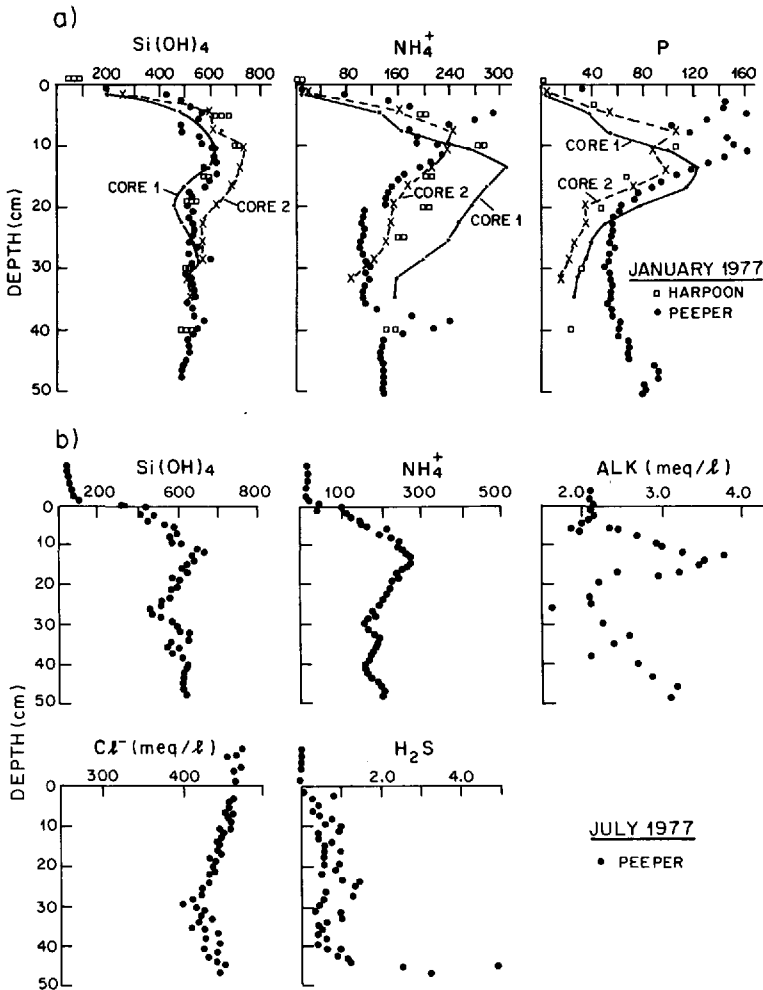


Figure 2. (a) Pore water profiles of silicate, ammonia, and phosphate sampled by core centrifugation, peeper and harpoon (see text) in January, 1977. (b) Pore water profiles of silicate, ammonia, alkalinity, chloride, and hydrogen sulfide sampled by peeper in July, 1977. Concentrations are $\mu\text{M}/\text{l}$ unless otherwise indicated.

maximum and then a decrease in concentration with depth rather than the approach to an asymptotic value. Dissolved iron data indicate that the top 10–15 cm are anoxic enough to maintain high levels of Fe(II), but below this depth the concentration decreases rapidly. Hydrogen sulfide values were undetectable (i.e., below $1 \mu\text{M}$) throughout the top 30 cm of the sediments.

Intercalibration results from cores, peeper, and harpoon are presented in Figure 2a. The difference in the concentrations of $\text{Si}(\text{OH})_4$, NH_4^+ , and P between the two cores is probably due to horizontal inhomogeneity (the cores having been approximately 1 m

apart) and is as great as differences among the sampling methods. The fine detail of the peeper shows zones of intense irrigation, indicated by reversals in the concentration gradients at 6 to 8 cm and below 15 cm. The spike in ammonia at 38 cm illustrates the intensity of localized reactions in these sediments.

The results from a peeper deployment later in the same year (Fig. 2b) indicate a dramatic minimum in silicate, ammonia, and alkalinity in the 20–30 cm depth interval. The chloride results show the degree of equilibration of the peeper which initially contained distilled water. The lack of total equilibration in chloride at around 30 cm could account for at most a 10% decrease in Si(OH)_4 , NH_4^+ , and alkalinity and thus cannot explain the concentration minima. Alkalinity concentrations in this region are nearly equal to bottom water values. Sulfide concentrations are near background values in the region 0 to 40 cm. It is clear, however, that sulfate reduction occurs above 20 cm and below 30 cm because of the highly elevated ammonia and alkalinity values (Rosenfield, 1981; Sholkovitz, 1973). The sediments are sufficiently irrigated with oxygen or the iron concentrations are sufficiently high in the top 40 cm to prevent substantial buildup of sulfide during sulfate reduction.

In August, 1978, pore waters were sampled using a peeper, a gravity core, and cores collected by diver, (Fig. 3). The diver cores resulted in data which are similar to those obtained previously although not as dramatic. The maxima in silicate, iron, and manganese occur in the top part of the peeper probably because it overpenetrated and was completely buried. The gravity core samples (Fig. 3b) reveal a very deep zone of irrigation—up to 70 cm—below which silicate values achieve their “asymptotic” concentration of about $850 \mu\text{M}$ and alkalinity increases as a result of sulfate reduction. Manganese concentrations drop to a value of $2\text{--}3 \mu\text{M}$ at 30 cm and remain at this level to the greatest depth penetrated—110 cm.

The winter sampling in 1979 (Fig. 4) revealed profiles of Si(OH)_4 , alkalinity, and iron(II) similar to those described previously. Copper, nickel, and cadmium trends are similar to silicate and alkalinity in that they go through a minimum at about 20 cm. The pore waters are highly enriched in these trace metals in the surface few centimeters and decrease both toward the sediment-water interface and with depth. The strongest vertical gradients, however, are in all cases, across the sediment-water interface.

There is a consistent pattern in the chemistry of the pore waters at this location in Puget Sound: the surface 10 to 15 cm are anoxic with alkalinity and ammonia values indicative of sulfate reduction and very high iron(II) and manganese(II) concentrations. Below this depth there is a dramatic decrease in the products of metabolism and reduced iron, manganese and trace metals. At about 50 cm the metabolic products of sulfate reduction again increase. Silicate profiles indicate that there is nondiffusive exchange with bottom water at irregular levels between 10 and 70 cm in the pore waters.

The pore water data imply that benthic animal activities are a dominant process in

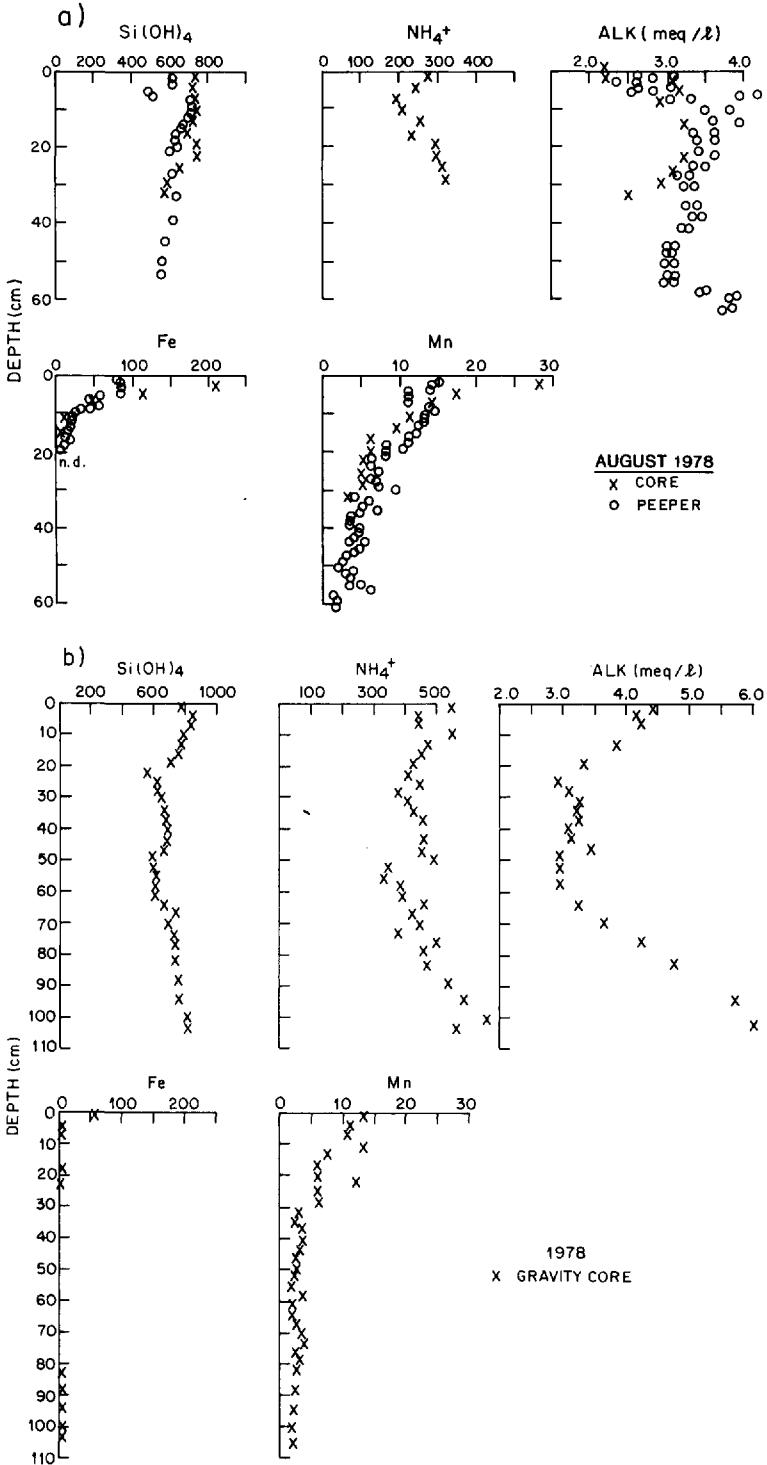


Figure 3. Pore water profiles of silicate, ammonia, alkalinity, iron, and manganese sampled in August, 1978 by (a) diver collected core with sediment centrifugation and a peeper, and (b) gravity core. Concentrations are $\mu\text{M/l}$ unless otherwise indicated.

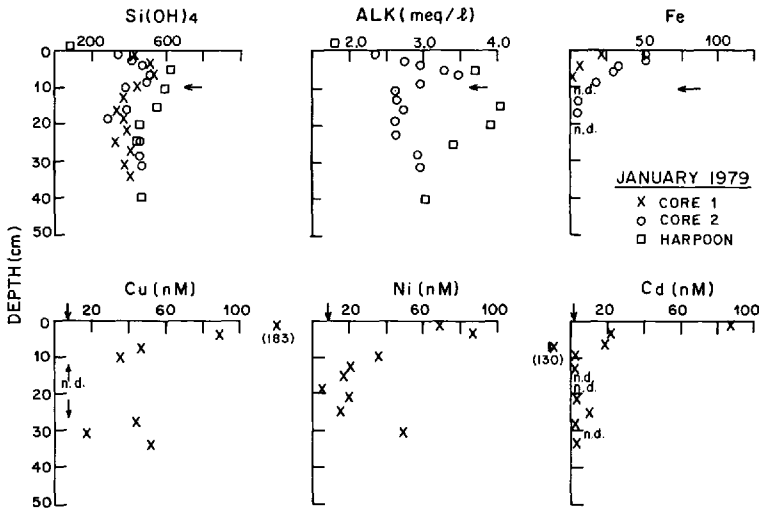


Figure 4. Pore water profiles of silicate, alkalinity, iron, copper, nickel, and cadmium sampled by coring and centrifugation in January, 1979. Arrows indicate bottom water values.

shaping the chemical distributions in the sediments at this location in Puget Sound. Their quantitative influence on the transport of dissolved chemical substances across the interface, however, is difficult to assess given the poor water data alone. The tritium experiments were designed to measure this value.

b. Tracer experiment. The results of the bell jar experiments are presented in Table 1 and Figure 5. Bottom water values measured at the termination of experiments B and C were higher than the added 50,000 T.U. (less than 10% of the added spike had penetrated the sediment pore waters). We believe that the most likely explanations for this result are that either the tritiated water in the bell jar was not well mixed when sampled or that the volume inside the bell jar was less than anticipated due to greater penetration into the sediments. Another potential problem is that the very top most flocculent portion of the sediment may not have been sampled during coring. These experimental difficulties cause uncertainty in the interpretation of the results, but are not fatal because we use the depth distribution of tritium in the sediments for the data analysis. To estimate the error associated with the bottom water activity uncertainties, we assumed that the process of ^3H penetration into the sediments was one-dimensional diffusion and calculated the required diffusion coefficient using the different estimates of the top boundary value. The different in the diffusion coefficient required to fit the data using different boundary concentrations was less than $\pm 50\%$. We take this value as our estimate of accuracy.

The most striking result of this experiment is the nearly exponential decrease in the tritium activity to nondetectable values at about 12 cm and then the increase above

Table 1. The results of the ^3H tracer experiments. The data are in tritium units (T.U.). The bottom water value inside the bell jar is designated B.W. (-) indicates the sample was lost during analysis. All data have been corrected for an analytical background of 70 T.U.

Experiment	Duration (s)	Depth (cm)	[^3H] (T.U.)		
A	60,300	0-2	24631		
		2-5	9089		
		5-8	1858		
		8-11	421		
		11-14	n.d.†		
		14-17	263		
		17-20	130		
		20-23	46		
		B	75,600	B.W.	73722
				0-2	8764
2-5	—				
5-8	3669				
8-11	301				
11-14	n.d.				
14-17	n.d.				
17-20	45				
23-26	n.d.				
26-29	n.d.				
C	95,000	29-32	n.d.		
		32-35	n.d.		
		B.W.	87598		
		0-4	—		
		4-7	1195		
		7-10	516		
		10-13	n.d.		

†n.d. means nondetectable.

background levels below this depth—in the region of 14–20 cm in two of the experiments (a background value of 70 T.U. has been subtracted from the data in Table 1). Clearly, these deep maxima indicate ^3H was entering the sediments by processes other than random motion of the pore water. In an experiment of the same type at the same location in 1981 we observed a similar result indicating the general nature of this finding (Bucholtz and Emerson, unpublished results). In the Discussion Section, we utilize these results in conjunction with the silicate pore water data to quantify transport of dissolved species in the sediments.

4. Discussion

The dominant burrow maker in the surface 20 cm of Quartermaster Harbor sediments is a cirratulid polychaete worm (P. Jumars, personal communication). We

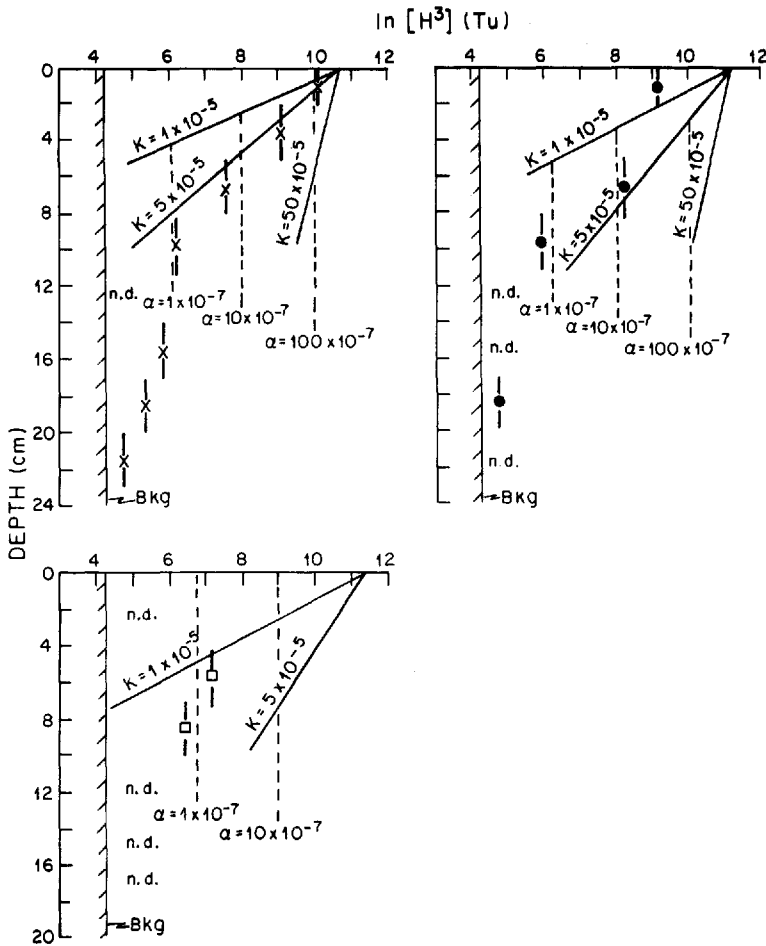


Figure 5. Natural log of the tritium concentration as a function of depth for three ^3H tracer experiments (see text). Solid lines are model fits for different values of the random mixing term, K with $\alpha = 0$. Dashed lines are model fits for different values of the “nonlocal” term, α with $K = 0$. n.d. = nondetectable.

have made no attempt to quantify their number or visually inspect their habitat. Deeper irrigation of the sediments, to 50 cm or more (Fig. 3), may be caused by burrowing thalassinid shrimp which are known to maintain very deep burrows and have also been identified in Puget Sound sediments (P. Jumars, personal communication). Further discussion of the benthic fauna at a deeper location in Puget Sound is presented in Grundmanis and Murray (1977).

In the following discussion we present a model to quantify the effect of animals on the transport of chemical species across the sediment-water interface using the ^3H

experiment and silicate pore water results. Our model is intended to describe the transport by animals in a very simple way with the goal of attempting to draw some first order generalizations regarding the effect of this process in shallow water estuarine sediments by comparing our results with those of other studies. An advantage of formulating the problem in the way presented here is that there is no need to evaluate the average microenvironment parameters such as burrow size and proximity to each other (Aller, 1980a), burrow membrane permeability (Aller, 1983; Aller *et al.*, 1983) or to assume that a single mechanism or animal causes the dominant department from molecular diffusion and reaction. The disadvantage of this approach is that the formulation requires the evaluation of an additional transport term which we must assume is identical for all chemical species. Aller (1980a, 1983) has shown that substances with reaction rates of different order respond differently to the effects of multidimensionality and burrow membrane permeability. Although these studies point out the potential artifacts in our approach, we believe it is important to propose a simple method for quantifying and generalizing, in a first order way, the effect of benthic animal activity on dissolved solute sediment-water transport in estuarine and nearshore sediments.

a. The model. We categorize pore water motion into two means of transport based on the characteristics of the pore water chemistry and upon previous studies of this subject (Aller, 1980b; Luedtke and Bender, 1974; Koresec, 1979). (1) The first transport mechanism is characterized as random motion and formulated as a diffusion process. The lower limit for the coefficient used to describe this process is molecular diffusion. Vanderborgh *et al.* (1977) use this type of model to interpret silicate pore water distributions modified by wave action along the Belgian North coast; Hammond *et al.* (1977) used it to predict the radon-222 flux from Hudson river sediments and Adler (1981) described ^{22}Na penetration into pore waters of MERL tanks in this way. (2) The second transport mechanism is analogous to pumping models described by Luedtke and Bender (1979), Hammond and Fuller (1979), Smethie *et al.* (1981) and Christensen *et al.* (1984). We represent this process as a "nonlocal" source or sink term (α) with dimensions of reciprocal time. This term was coined by Imboden (1981) and means simply any mode of transport that is capable of exchanging material between nonadjacent points in the sediment or between the overlying water and points in the sediment removed from the sediment-water interface.

Mathematically the problem is formulated as one-dimensional diffusion with a nonlocal term and reaction:

$$\frac{\partial C}{\partial t} = K \frac{\partial^2 C}{\partial z^2} - \alpha(C - C_0/\phi) + R. \quad (1)$$

Advection is not included because in this environment sedimentation is very slow compared to the other transport mechanisms. K is the coefficient used to describe

random motion (note that K as described here is depth independent and includes the corrections necessary for tortuosity, i.e., in the case where K is a molecular diffusion coefficient, $K = D_s$, the bulk sediment diffusion coefficient, Berner, 1970) and α is the rate parameter used to evaluate the nonlocal source or sink. In keeping with the intended simplification of the problem, we characterize this parameter as depth independent. Although a glance at the pore water data indicates that this is a clear abstraction from reality, we opt to evaluate the range of values in α necessary to describe the data rather than to derive the detailed depth dependency. C_0 in the above equation is the concentration of the dissolved substance in the overlying water, ϕ is porosity and R is the reaction rate term. Boundary conditions and the reaction rates are different for different chemical species and are presented below. The physical significance of the nonlocal model in terms of the two dimensional cylindrical co-ordinate system problem of Aller (1980a) can be shown mathematically (B. Boudreau, this issue).

b. Evaluation of the transport parameters. We use the tracer experiment and the distribution of silicate in the pore waters to evaluate the mixing parameters, K , and α . The time course of tritium penetration into the sediments is described by Eq. (2) with $R = 0$ and the assumption that the sediments are infinitely deep and the tritium concentration in the overlying water does not change with time (the latter approximation is valid for small t); thus,

$$\frac{\partial [^3\text{H}]}{\partial t} = K \frac{\partial^2 [^3\text{H}]}{\partial z^2} - \alpha([^3\text{H}] - [^3\text{H}]_0)/\phi \quad (2)$$

with the boundary and initial conditions:

$$\begin{aligned} \text{at } z = 0 \text{ and } t > 0 & \quad [^3\text{H}] = [^3\text{H}]_0/\phi \\ \text{at } z > 0 \text{ and } t = 0 & \quad [^3\text{H}] = 0 \end{aligned} \quad (3)$$

The solution to this equation is

$$[^3\text{H}] = [^3\text{H}]_0/\phi - ([^3\text{H}]_0/\phi) e^{-\alpha t} \operatorname{erf}\left(\frac{z}{2(Kt)^{1/2}}\right). \quad (4)$$

The predicted tritium depth distribution for the boundary conditions and times listed in Table 1 and various values of K and α are presented along with the data in Figure 5. The effect of increasing K is to decrease the slope of the predicted concentration-depth profile with the intercept at $z = 0$ equal to the bell jar value. The effect of increasing α is to increase the depth independent ^3H contribution from the nonlocal source. There are two possible interpretations of the data above the deep maxima (1) a mixing coefficient of $4 \pm 1 \times 10^{-5} \text{ cm}^2/\text{s}$ with no nonlocal term would adequately describe the results. The self diffusion coefficient of water at 10°C is $1.4 \times 10^{-5} \text{ cm}^2/\text{sec}$ (Simpson

and Carr, 1958). To compare this value with K it must be adjusted for the effects of tortuosity. As a first approximation, tortuosity can be estimated to be $\phi^{1.5}$ to $\phi^{2.0}$ times the free diffusion coefficient in high porosity muds (Ullman and Aller, 1982). The porosity in the surface sediments is ~ 0.9 ; thus, the molecular diffusion coefficient of tritiated water in these sediments at 10°C is $1.1 \times 10^{-5} \text{ cm}^2/\text{sec}$. The value required to explain the results is 3–5 times the molecular value. (2) An alternate explanation for the results is molecular diffusion with a nonlocal source parameter, α , between $1 \times 10^{-7} \text{ s}^{-1}$ and $10 \times 10^{-7} \text{ s}^{-1}$. Since α may decrease with depth, one could explain the exponentially decreasing $[^3\text{H}]$ between 0 and 15 cm by a depth dependent value in the range given above. In the following discussion we use the silicate profiles as an aid in distinguishing the two possible interpretations of the tritium results.

To describe silicate profiles in the sediments we assume steady state and that the dissolution of diatoms is first order with respect to the difference between the local concentration and the asymptotic value (Hurd, 1973). The first order rate constant is, k . Eq. (2) becomes:

$$0 = K \frac{d^2[\text{Si}]}{dz^2} - \alpha([\text{Si}] - [\text{Si}]_0/\phi) + k([\text{Si}]_a - [\text{Si}]) \quad (5)$$

or

$$0 = K \frac{d^2[\text{Si}]}{dz^2} - (k + \alpha)[\text{Si}] + k[\text{Si}]_a + \alpha[\text{Si}]_0/\phi$$

For the boundary conditions:

$$\begin{aligned} \text{at } z = 0, [\text{Si}] &= [\text{Si}]_0/\phi \\ \text{at } z = Z_1, \left. \frac{\partial[\text{Si}]}{\partial z} \right|_{z_1} &= G \end{aligned} \quad (6)$$

where G is the gradient in $[\text{Si}(\text{OH})_4]$ at $z = Z_1$

The solution is:

$$\begin{aligned} [\text{Si}](z) = & \left(\frac{k[\text{Si}]_a + \alpha[\text{Si}]_0/\phi}{\beta} \right) (1 - e^{\gamma z}) + ([\text{Si}]_0/\phi) e^{\gamma z} + \frac{G \sinh(\gamma z)}{\cosh(\gamma Z_1)} \\ & + \frac{e^{\gamma(z+Z_1)} - e^{-\gamma(z-Z_1)}}{\cosh(\gamma Z_1)} \left(\frac{k[\text{Si}]_a + \alpha[\text{Si}]_0/\phi}{\beta} - [\text{Si}]_0/\phi \right) \end{aligned} \quad (7)$$

where:

$$\gamma = (\beta/K)^{1/2}$$

and

$$\beta = (k + \alpha).$$

Table 2. Values of the parameters used in the silicate model and their source. k = opal dissolution rate; D = $\text{Si}(\text{OH})_4$ molecular diffusion coefficient; $[\text{Si}(\text{OH})_4]_o$ = bottom water silicate concentration; $[\text{Si}(\text{OH})_4]_a$ = "asymptotic" pore water silicate concentration. Note that four different estimates for k are within a factor of three of each other at 10°C .

Parameter	Value ($^\circ\text{C}$)	Source	Value at 10°C †
k (s^{-1})	2.0×10^{-7} (11°C)	Laboratory diatom dissolution (Grill and Richards, 1964)	2.0×10^{-7}
	1.2×10^{-7} (3°C)	Deep Sea Pore Water (Hurd, 1973)	$2.4\text{--}3.0 \times 10^{-7}$
	5.0×10^{-7} (10°C)	North Sea Pore Water (Vanderborgh <i>et al.</i> , 1977)	5.0×10^{-7}
	23×10^{-7} (29°C)	Mud Bay, S.C. Pore Water (Aller, 1980a)	$2.4\text{--}4.2 \times 10^{-7}$
	10×10^{-6} (25°C)	(Wollast and Garrels, 1971)	7.0×10^{-6}
D ($\text{cm}^2 \text{ s}^{-1}$)			
$[\text{Si}(\text{OH})_4]_o$	$70 \times 10^{-6} \text{ M}$	measured in Puget Sound	
$[\text{Si}(\text{OH})_4]_a$	$850 \times 10^{-6} \text{ M}$	measured in Puget Sound	

† Assuming (a) the activation energy for the dissolution rate constant is $-(15 \text{ to } 20) \text{ Kcal mole}^{-1}$ (Aller and Benninger, 1983); (b) The diffusion coefficient halves for a temperature change of 25°C to 0°C .

Values for the parameters $[\text{Si}]_o$, $[\text{Si}]_a$, k , and $D_{\text{Si}(\text{OH})_4}$ are listed in Table 2. The first order rate coefficient, k , has been evaluated in laboratory experiments and by fitting pore water data. Recent estimates are presented in the table and adjusted to the temperature of Quartermaster Harbor sediments using published activation energy data. The values fall between 2 and $5 \times 10^{-7} \text{ s}^{-1}$ for 10°C . This range encompasses the four independently reported values and we believe it can be accepted with some degree of certainty. The molecular diffusion coefficient for silicate at 25°C is $10 \times 10^{-6} \text{ cm}^2/\text{sec}$ (Wollast and Garrels, 1971). Since diffusion coefficients roughly double for every 25°C temperature increment (Li and Gregory, 1974), we estimate a value of $7 \times 10^{-6} \text{ cm}^2/\text{s}$ at 10°C . The correction for tortuosity ($\phi^2 \sim 0.8$) brings the value for $\text{Si}(\text{OH})_4$ diffusion in the sediments to $\sim 5 \times 10^{-6} \text{ cm}^2/\text{s}$ or nearly ten times less than the enhanced value of K required to describe the tritium distribution if the "nonlocal" term is zero. The value of $[\text{Si}]_a$ was determined from the deep concentration derived from the gravity core (Fig. 3). The bottom boundary (Z_1) was set at 20 cm and the value used for G (Eq. 6) was zero.

$[\text{Si}(\text{OH})_4]$ profiles derived from Eq. (7) for different values of K and α are presented along with data derived from the peepers in Figure 6. The very interesting result that emerges from this analysis is that the silicate profile near the sediment-water interface can be reproduced only if the molecular diffusion coefficient ($5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) is used for K . For the enhanced diffusion rate of $5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (one of the possible explanations for the tritium results) to fit the silicate data would require a dissolution

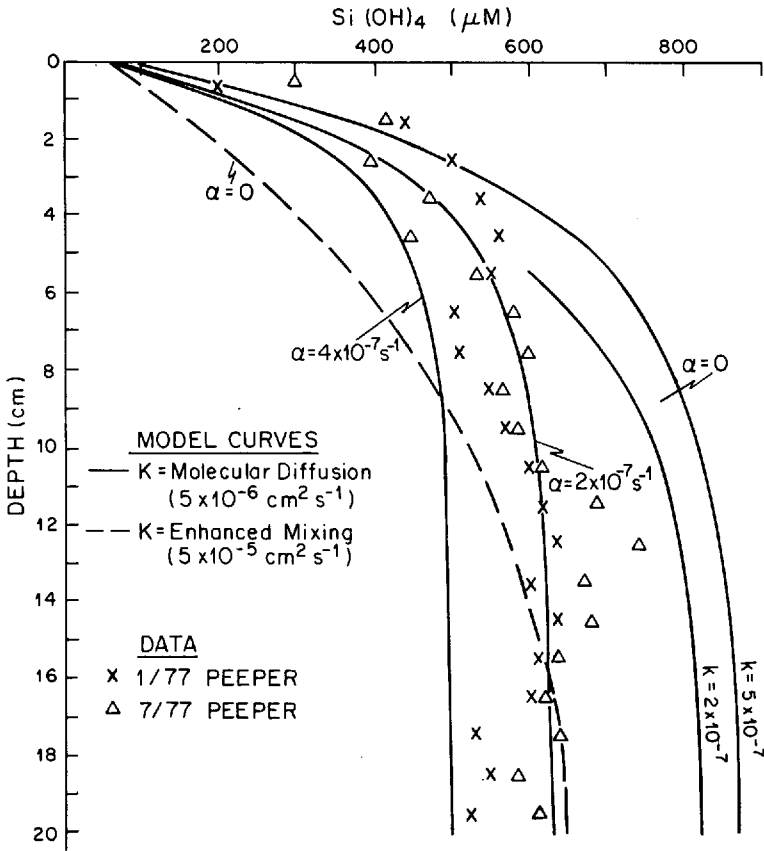


Figure 6. Model solutions for the depth distribution of silicate for enhanced mixing ($D = 5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) with no nonlocal transport ($\alpha = 0$), and molecular diffusion ($D = 5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) with three different values of the nonlocal term ($\alpha = 0, 2, 4, \times 10^{-7} \text{ s}^{-1}$). The opal dissolution rate, k , is assumed to be $5 \times 10^{-7} \text{ s}^{-1}$ except where indicated. The bottom boundary (Z_1) is 20 cm and the boundary condition is $(dc/dz)_{z_1} = 0$. Si(OH)_4 data from peeper samples are shown for comparison.

rate constant ten times the best estimate of $2-5 \times 10^{-7} \text{ s}^{-1}$ which is outside the range of error for this value.

The only unique explanation for both the results of the tritium experiment and the silicate data is that molecular diffusion dominates the random motion transport near the sediment-water interface and a "nonlocal" term is required for tritium to penetrate to the depths observed and for the slow approach of $[\text{Si(OH)}_4]$ to its asymptotic value. The magnitude of the nonlocal term necessary to explain the silicate data is evaluated in Figure 7 which shows the calculated concentration of $[\text{Si(OH)}_4]$ at 15–20 cm as a function of α and the silicate dissolution rate, k . Measured values are between 500 and

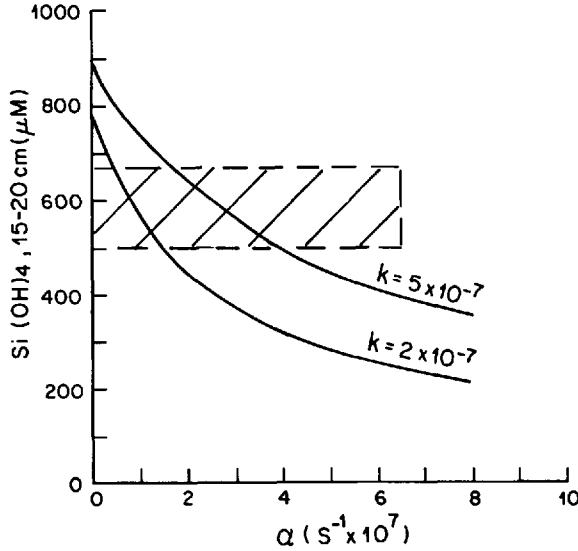


Figure 7. The model predicted Si(OH)_4 concentration at $Z = 15\text{--}20$ cm as a function of the opal dissolution parameter, k , and the nonlocal parameter, α . The hatched area indicates the range observed in Puget Sound sediments. Si(OH)_4 asymptotic = $850 \mu\text{M}$, $\text{Si(OH)}_{4,z=0} = 70 \mu\text{M}$, $D = 5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

$700 \mu\text{M/l}$ requiring a nonlocal term of between 1 and $4 \times 10^{-7} \text{ s}^{-1}$ for the accepted dissolution rates. The depth dependence of α is by no means totally random. The tritium results suggest a value of $\sim 10 \times 10^{-7}$ in the $2\text{--}8$ cm depth interval, and both tritium and silicate data indicate more active communication between pore water and bottom water below $\sim 12\text{--}14$ cm than immediately above (i.e., the H^3 peak at $14\text{--}20$ cm in experiments A and B and the persistent minimum in Si(OH)_4 below 15 cm). The latter result may be due to the geometry of worm burrows which are sometimes U-shaped (e.g. McCaffrey *et al.*, 1980; Davis and Miller, 1979) thus providing more effective ventilation of the sediments at the horizon of the bottom of the burrow. In any case, α appears to go through a minimum at $10\text{--}15$ cm allowing the $[\text{Si(OH)}_4]$ concentration to reach a maximum at this depth.

The depth to which equal concentrations of tritium would penetrate by molecular diffusion and by a nonlocal term of $10 \times 10^{-7} \text{ s}^{-1}$ is 2.5 cm in ~ 18 hours (Fig. 6a). Only one data point ($2\text{--}5$ cm of tritium experiment A) falls outside the interpretation requiring molecular diffusion to dominate the dissolved species transport above this depth and the nonlocal mechanism to dominate below.

c. Dissolved fluxes across the sediment-water interface. The problem of abstracting dissolved transport in sediments from the operating mechanism to a simple but universal model is that the transport parameters, α and K in our case, are strictly unique only to the tracer from which they are derived. The main reasons for this derive

from the model simplifications and the different chemical properties of the dissolved species. Aller (1983) and Aller *et al.* (1983) have recently shown that burrow membrane permeabilities to Si(OH)_4 and NH_4^+ differ by a factor of ~ 2 – 3 , but that there could be a very great difference between small inorganic molecules and larger organic species and their complexes. We believe also that the greatest potential source of error in the calculation of fluxes which follows is in the assumption that none of the solutes considered is substantially complexed by high molecular weight dissolved organic matter.

To evaluate the influence of animal activity on sediment-water exchange, we compare the fluxes across the sediment-water interfaces resulting from diffusion and the nonlocal mechanism. The data in Figures 1–4 and the integrated form of the first two terms on the right side of Eq. (1) are used in the calculations (see Table 3). Diffusion fluxes are lower limits in cases where peepers were not the sampling method because of the relatively large pore water sampling interval. For the nonlocal estimate we assume that $\alpha = 3 \pm 2 \times 10^{-7} \text{ s}^{-1}$ and that it operates over the top 20 cm of the sediments. These assumptions probably also produce a lower limit of the flux because they may underestimate the value of α in the top few cm (see Fig. 5) and assume a minor contribution from below 20 cm. The results in Table 3 indicate that nonlocal transport dominates the flux in Quartermaster Harbor for species which do not have very strong gradients at the sediment-water interface. This is true especially for alkalinity but also holds for ammonia and silicate. For the metals, nonlocal transport dominates only for nickel which has a relatively deep maximum (Fig. 4); iron and manganese fluxes are of the same magnitude by both mechanisms and the fluxes of cadmium and copper are mainly due to molecular diffusion because of the strong enrichment in the surface pore waters. It is likely that a significant fraction of the copper, and perhaps other trace metal concentrations in the pore waters are present as complexes with dissolved organic matter (Elderfield and Hepworth, 1975). In this case, fluxes may be overestimated because of the dependency of the molecular diffusion coefficient on molecular weight (Elderfield, 1981).

The effect of animal activity on sediment-water fluxes of Si(OH)_4 , NH_4^+ and alkalinity relative to molecular diffusion is less than that reported for San Francisco Bay by Hammond and Fuller (1979) and somewhat greater than that observed in Narragansett Bay (McCaffrey *et al.*, 1980) and Long Island Sound (Aller and Benninger, 1983). In the latter study, comparison of direct measurements of silicate benthic fluxes with calculated fluxes using pore water gradients indicated that fluxes were usually controlled by molecular diffusion, however, enhanced transport was suggested in locations with active benthic animal activity. Quartermaster Harbor is a shallow water productive embayment in Puget Sound and may not be typical of the deeper locations where the organic carbon flux to the sediments is probably less. For this reason we cannot say the mechanisms and fluxes reported here are representative of the Sound.

Because it is near shore, Quartermaster Harbor is typical of an estuarine environ-

Table 3. Flux estimates between bottom water and pore water for the two main transport mechanisms: molecular diffusion and nonlocal transport. D/NL is the ratio of diffusion flux to nonlocal flux. The range in this value is caused by the range in the estimate of $\alpha(1-5 \times 10^{-7})$. Bottom water values are: $[\text{Si}(\text{OH})_4] = 70 \mu\text{M}$; $[\text{NH}_4^+] = 0 \mu\text{M}$; $\text{Alk} = 2.1 \text{ meq/l}$; $[\text{Fe}]$ and $[\text{Mn}] = 0 \mu\text{M}$; $[\text{Cu}] = 6 \text{ nM}$; $[\text{Ni}] = 8 \text{ nM}$; $[\text{Cd}] = 0.3 \text{ nM}$.

Species	Date	Gradients and totals		Fluxes		D/NL
		$\partial C/\partial Z _{z=0}$ ($\text{m cm}^{-4} \times 10^9$)	$\int_0^{15} C dZ$ ($\text{m cm}^{-2} \times 10^6$)	Diffusive† ($\text{m cm}^{-2} \text{ s}^{-1} \times 10^{-5}$)	NonLocal‡	
Si(OH) ₄	7/76	106	11.50			
	1/77	245	10.6			
	7/77	200	11.3			
	8/78	270	13.0			
	1/79	250	8.0			
	AVE.	214 ± 66	10.0 ± 1.8	1071 ± 328	948-4740	0.23-1.1
NH ₄ ⁺	7/76	70	7.0			
	1/77	60	3.5			
	7/77	83	7.8			
	8/78	42	4.7			
	AVE.	64 ± 17	5.7 ± 2.0	574 ± 155	575-2875	0.20-1.0
Alk	7/77	100	50			
	8/78	167	65			
	7/79	285	55			
	AVE.	184 ± 94	5.7 ± 8.0	1104 ± 562	5666-28333	0.04-0.19
Fe ²⁺	7/76	50	1.12			
	8/78	75	0.08			
	1/79	25	0.31			
	AVE.	50 ± 25	0.7 ± 0.4	200 ± 100	70-350	0.57-2.9
Mn ²⁺	8/78	15	0.288	60	29-145	0.41-2.1
Cu	1/79	0.12	0.850×10^{-9}	0.49	0.80-42	1.20-5.8
Ni	1/79	0.03	1.05×10^{-9}	0.12	0.10-0.5	0.24-1.2
Cd	1/79	0.04	0.28×10^{-9}	0.18	0.03-0.14	1.3-6.0

† $F = \phi D_s dC/dz|_{z=0}$ Diffusion coefficients are for 10°C and tortuosity = ϕ^2 , where $\phi = 0.9$, (see text); $D_{\text{Si}} = 5 \times 10^{-6}$; $D_{\text{NH}_4^+} = 9 \times 10^{-6}$; $D_{\text{HCO}_3^-} = 6 \times 10^{-6}$; $D_{\text{metals}} = 4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

‡ $F = \alpha(\int_0^{20} \phi C dZ - C_{B.W.} \Delta z)$ where $C_{B.W.}$ is the bottom water concentration; $\Delta z = 20 \text{ cm}$ and $\alpha = 3 \pm 2 \times 10^{-7} \text{ s}^{-1}$. The range in F is due to the range in α .

ment likely to receive trace metal pollution from anthropogenic sources (i.e., arsenic, Carpenter *et al.*, 1978). Enhanced ventilation of the sediments by biological activity in this location affects the distribution of trace metals in the sediments in two important ways. (1) Nonlocal transport provides an additional exchange mechanism with the bottom waters, and (2) facilitated ventilation of the sediments with bottom water alters the chemistry of the redox species iron, manganese and sulfur. Removal of sulfide in the surficial 10 cm of sediments by oxidation with oxygen would facilitate the mobilization of Cu and Cd (and other class B metals) which form very insoluble sulfides (Emerson *et al.*, 1983; Jacobs and Emerson, 1982). The combined effect of

these mechanisms is to enhance the role of the sediments as a source of dissolved trace metals to the overlying waters.

Elderfield *et al.* (1981) presented one of the few other examples of trace metal analysis in estuarine pore waters. In Narragansett Bay sediments, the concentrations of Ni and Cd were below bottom water concentrations in the surface pore waters and below detection limits a few centimeters beneath the sediment-water interface. Copper exhibited a maximum in the top few centimeters of the interstitial waters. They attributed the generally low concentrations of the trace metals to insoluble sulfide formation. The sediments of Narragansett Bay, thus, act as a sink for nickel and cadmium and a source for copper. In Quartermaster Harbor the sediments are a source for all three metals perhaps because of the effective ventilation by animal activity.

5. Conclusions

Using a combination of an *in situ* ^3H exchange experiment and pore water silicate data we show that transport processes in sediment pore waters of Quartermaster Harbor in Puget Sound are dominated by molecular diffusion in the top few centimeters with animal activity being the most important transport process below this (to 20–70 cm). The value of the transport parameter for the nonlocal process is $1\text{--}5 \times 10^{-7} \text{ s}^{-1}$. Using this value and pore water concentrations it can be demonstrated that animal activities are the dominant process driving sediment-water dissolved fluxes except for elements with dramatic bottom water-pore water concentration gradients.

One of our goals in this work is to test the feasibility of generalizing about animal burrowing and respiratory mechanisms which affect sediment-water dissolved fluxes in near shore marine environments. In Table 4 we list previously determined transport parameters along with the tracer and model used. Where possible the value is converted to the equivalent nonlocal parameter. With the exception of two values, the data are encompassed by nonlocal parameter values of $1\text{--}20 \times 10^{-7}$. The very high values from the Washington Continental shelf ($\sim 100 \times 10^{-7} \text{ s}^{-1}$, Smethie *et al.*, 1981) are from the mouth of the Columbia River and may be caused by bottom current rather than benthic animal activity. The high value from San Francisco Bay ($87 \times 10^{-7} \text{ s}^{-1}$, Hammond and Fuller, 1979) is calculated from radon deficiencies and represents the top 0–4 cm. Thus, it should be compared with the high range of the values in the Table, but is, nonetheless, significantly greater than the other estimates.

Nearshore sediment-water transport by animal activities varies by less than two orders of magnitude in five different environments on the west and east coasts of the United States (Table 4). The influence of benthic animal activity on the pore water flux depends greatly upon the depth at which the element is released to the pore waters. For trace metals in shallow, productive, nearshore waters the main influence is probably indirect, in that the enhanced sediment ventilation inhibits the build up of sulfide in the pore waters, thus preventing metal sulfide formation and increasing the solubility of the metals in the near surface pore waters.

Table 4. Literature values for dissolved solute transport in nearshore and estuarine sediments caused by nondiffusive mechanisms. The literature-derived transport parameter was converted to the equivalent nonlocal term when possible.

Location (Author)	Tracer	Model	Transport coefficient	Equivalent "nonlocal" term (s ⁻¹)
Hudson River (Hammond <i>et al.</i> , 1977)	²²² Rn	mixing	12 × 10 ⁻⁵ (cm ² s ⁻¹)	—
Puget Sound, 200 m (Grundmanis and Murray, 1977)	Si(OH) ₄	nonlocal		0.5–1.0 × 10 ⁻⁷ *
San Francisco Bay (Hammond and Fuller, 1979)	²²² Rn	pumping (0–4 cm)	3 cm d ⁻¹	87 × 10 ⁻⁷
Narragansett Bay (Luedtke and Bender, 1979)	²² Na	pumping (non local)	.04–11 d ⁻¹	5–13 × 10 ⁻⁷
Mud Bay, South Carolina (Aller, 1980a)	Si(OH) ₄ NH ₄ ⁺	Cylindrical diffusion	—	13 × 10 ⁻⁷ †
MERL tanks, R.I. (Adler, 1981)	²² Na	diffusion (0–5 cm)	7 × 10 ⁻⁵	—
Washington Continental Shelf (Smethie <i>et al.</i> , 1981)	²²² Rn	pumping (0–5 cm)	0.2–4.4 (cm d ⁻¹)	4–100 × 10 ⁻⁷ ‡
Washington Continental Shelf (Christensen <i>et al.</i> , 1984)	sulfate re- duction	irrigation coefficient (2–10 cm)	.05–0.8 (cm ⁻²)	2–31 × 10 ⁻⁷
	²²² Rn		0.15–0.55 (cm ⁻²)	5–17 × 10 ⁻⁷
Puget Sound, 15M (this work)	³ H Si(OH) ₄	non local		1–5 × 10 ⁻⁷

*Si(OH)₄ data from Grundmanis and Murray (1977) and the reaction rate constant at 10°C were used to evaluate the nonlocal term.

†The Si(OH)₄ data and reaction rate constant in Aller (1980a) were used to derive the nonlocal term.

‡The high value (100 × 10⁻⁷ s⁻¹) is from data at the mouth of the Columbia River. (see text.)

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