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Spatial and temporal patterns of dissolved ammonium, manganese, and silica fluxes from bottom sediments of Long Island Sound, U.S.A.

by Robert C. Aller¹ and Larry K. Benninger^{2, 3}

ABSTRACT

The flux of dissolved NH_4^+ , Mn^{2+} , and Si(OH)_4 from bottom sediments was measured directly at 14 stations throughout central and western Long Island Sound, U.S.A. Comparisons at three stations show that NH_4^+ and Si(OH)_4 fluxes generally agree within a factor of ~ 2 or better with those calculated from pore water solute gradients. Si(OH)_4 fluxes are also consistent with reported opaline silica dissolution rates. Seasonal measurements at three stations show that fluxes vary directly with temperature and are highest in summer. NH_4^+ and Si(OH)_4 fluxes are characterized by 'apparent activation energies' of 18 ± 3 Kcal/mole consistent with the temperature dependence of their production reactions. Net Mn^{2+} fluxes show a more variable temperature dependence of 35 ± 15 Kcal/mole, apparently due to precipitation reactions within the sediment.

The summer fluxes ($T = 20\text{-}22^\circ\text{C}$) of all three solutes reflect depositional environment and correlate directly with the quantity of fine-grained material and percent organic matter in surface sediment. In addition, NH_4^+ fluxes are slightly depth dependent: the ratio of NH_4^+ released to organic matter present in the sediment decreases with increasing water depth. The total range of fluxes was -1 to 8 , -0.6 to 4 , and 0 to 20 mmol/m²/day for NH_4^+ , Mn^{2+} , and Si(OH)_4 , respectively. Average yearly benthic solute fluxes are comparable to or greater than lateral water column transport of solutes into the basin. The average yearly NH_4^+ flux from the bottom can supply at least 20-25% of the daily N requirement of plankton although substantial local variation in importance is likely.

Muddy regions of high solute release also have high excess ²³²Th inventories, demonstrating extraction of reactive elements from the water column into the same areas. The muddy interior of the basin away from the mouth is therefore a particularly interactive and important sub-region of the estuary with respect to controlling water column composition.

1. Introduction

The constant reflux of solutes and particles between bottom sediments and their overlying waters is an important component of material cycles determining biologi-

1. Department of the Geophysical Sciences, University of Chicago, 5734 S. Ellis Ave., Chicago, IL, 60637, U.S.A.

2. Department of Geology and Geophysics, Yale University, New Haven, CT, 06520, U.S.A.

3. Present address: Department of Geology, University of North Carolina, Chapel Hill, NC, 27514, U.S.A.

cal activity and chemical composition of aquatic environments. For example, in nearshore marine regions soluble nitrogen compounds released from the seafloor during the decomposition of organic matter can supply 30-100% of the dissolved N taken up daily by phytoplankton in overlying water (Davies, 1975; Rowe *et al.*, 1975; Hartwig, 1976; Nixon *et al.*, 1976; Billen, 1978). Sedimentary metals such as Mn or Fe are also solubilized during organic matter decomposition and can diffuse out of the bottom. As a result, Mn^{++} and Fe^{++} continuously reprecipitate onto suspended particles in the oxidized water column and are redistributed within depositional basins (Evans *et al.*, 1977; Turekian, 1977; Grill, 1978; Murray and Gill, 1978; Yeats *et al.*, 1979). The exact pattern of metal redistribution or influence on biological productivity due to sediment-water fluxes reflects the particular balance between solute release rates from sediments, precipitation or biological uptake kinetics in the water column, and water circulation within different regions of an environment. In this report, we emphasize one aspect of these processes and examine the spatial and, to a lesser extent, temporal release patterns of solutes from sediments of a single estuarine basin, Long Island Sound, U.S.A. We concentrate on the biogeochemically important species: NH_4^+ , Mn^{++} , and $Si(OH)_4$. In addition, measurements of excess ^{234}Th in bottom sediments at many stations (Aller *et al.*, 1980), allow documentation of the relative reactivity of different areas with respect to sediment-water exchange of particles as well as solutes.

Study area. Long Island Sound is an estuarine trough trending east-west along the northeast coast of North America (Fig. 1). The Sound is approximately 150 km long and varies in width from 5 to 40 km. Water depths range to a maximum of ~ 100 m at the easternmost passages and average ~ 20 m overall. The bottom slopes to the south in the central basin, producing relatively deep water (~ 40 m) close to the Long Island coast. Salinity varies from ~ 24 to 28‰ and temperature oscillates seasonally in a sinusoidal fashion from ~ 2° to 22°C (Riley, 1956).

Sediment is predominately sand-size east of 72°40'W and in a narrow band along the coastline (McCrone *et al.*, 1961; Buzas, 1965; Bokuniewicz *et al.*, 1976). Sand also accumulates as isolated shoal features. Silt-clay size material dominates the central and western portions and covers about 60% of the total area of the Sound (Bokuniewicz *et al.*, 1976).

Sampling and methods. Estimates of NH_4^+ , Mn^{++} , and $Si(OH)_4$ fluxes from bottom sediments were made by incubating undisturbed box cores and their immediately overlying water for short periods after collection. The rate of change of solute concentration in the overlying water is taken as a measure of the net release rate from the bottom. This incubation technique has been used by many investigators and, in shallow water environments, gives results comparable to *in situ* measurements (Pamatmat, 1971; Davies, 1975; Nixon *et al.*, 1980; McCaffrey *et al.*, 1980). Specifics are given below.

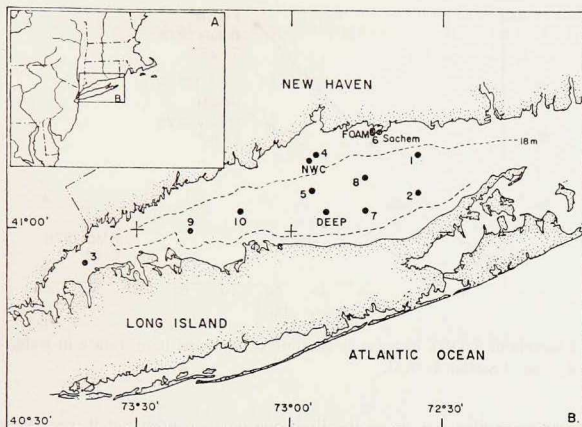


Figure 1. (A). Location of Long Island Sound on east coast of North America. (B). Location of stations at which flux measurements were made.

Core samples were taken from 14 stations located throughout the Sound (Fig. 1). In all cases, cores were obtained by divers using handheld acrylic box corers (Aller, 1980a). Corers used for estimating fluxes were of two sizes and sample bottom surface areas of either 222 or 300 cm². Boxes were gently inserted ~ 10 to 15 cm into the bottom and relatively undisturbed sediment samples retrieved with overlying water volumes of 2 to 5 liters. These samples were returned to the surface, their temperature recorded using a thermometer, and then placed into coolers for temporary storage before processing.

Cores for seasonal studies were taken at three stations in the central Sound, FOAM, NWC, and DEEP, from summer 1975 through winter 1976 (Fig. 1). Samples from an additional nearshore station, SACHEM, were also obtained in summer 1975. These stations are from subregions representative of the range of physical environments and benthic communities found in the central basin (Aller, 1980a). In each case a single box core (300 cm² area) and a corer containing only water to serve as a control were returned to shore and incubated in the dark at 22° (summer), 15° (fall), or 4° (winter-spring) depending on bottom water temperature at the time of collection. Water overlying the cores was periodically aerated and successively sampled, after stirring, over one day (summer cores) to seven day (winter cores) periods depending on temperature and expected magnitude of solute flux. The first water sample was taken 3-4 hours after core retrieval.

Pore water solute concentration gradients in additional box cores from these

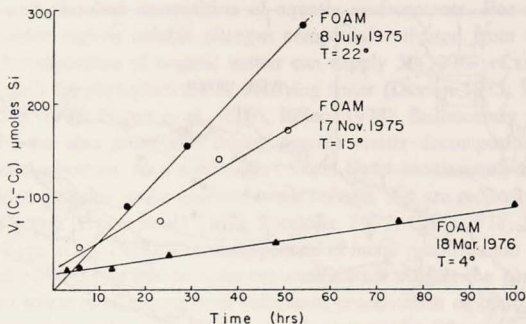


Figure 2. Example of Si(OH)_4 increase as function of time and temperature in water overlying box cores taken at Station FOAM.

three stations were also measured to allow comparison with net fluxes. Most of the resulting data together with seasonal NH_4^+ and Mn^{++} fluxes at FOAM, NWC, and DEEP are reported in detail elsewhere (Aller, 1980a, b); however, dissolved Si(OH)_4 pore water profiles for fall 1975 and winter 1976 not previously reported for these stations are given here for the first time, along with estimates of seasonal net Si(OH)_4 fluxes. Sample handling for pore water separations is described in Aller (1980a) and is summarized as follows. Box cores were placed in a glove bag, sampled under N_2 at 1-3 cm intervals, and pore water separated by squeezing (Kalil and Goldhaber, 1973). Cores collected during the winter were squeezed at 4°C using cooling jackets described by Kalil and Goldhaber (1973); fall cores were squeezed at room temperature (~22°C). Water was expressed through 0.45 μm pore size Millipore filters after passing through a glass fiber pre-filter. No measurable Si blank was found due to use of the pre-filter.

A second set of cores for flux estimates from 10 additional stations were collected during the period July 21, 1977 to August 8, 1977 (Fig. 1). Because of previous findings that no significant change in solute concentration took place in control corers containing water alone, no controls were collected at this time but rather two replicate sediment cores at each station were used instead. Cores were stored in the dark and usually in coolers. Water overlying the cores was sampled using syringes on board the diving boat. One sample was taken within one hour of collection and a second water sample 3 to 6 hours later. In three cases a third sample was taken on shore 6-10 hours after collection. Cores may have warmed slightly during incubation but this was not explicitly checked; air and water temperatures are usually within 1-3°C of each other at this time of year (e.g. Riley, 1956).

Water samples were immediately filtered through 0.4 μm pore size Nuclepore

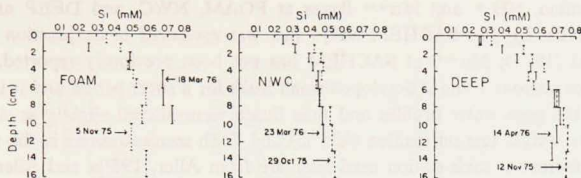


Figure 3. Pore water $\text{Si}(\text{OH})_4$ profiles at FOAM, NWC, and DEEP during fall 1975 (dashed lines) and winter-spring 1976 (solid lines). Overlying water concentrations are $\lesssim 26 \mu\text{M}$ (Table 2).

filters into acid rinsed polyethylene bottles. One aliquot was acidified and used later for Mn^{++} and $\text{Si}(\text{OH})_4$ determinations; a second was left unacidified and used for NH_4^+ analysis.

Mn^{++} was determined colorimetrically using formaldoxime without Fe correction (Goto *et al.*, 1962). Separate Fe analyses demonstrated that correction was unnecessary. NH_4^+ was measured using phenolhypochlorite (Solorzano, 1969) and $\text{Si}(\text{OH})_4$ by use of the reduced molybdate method (Strickland and Parsons, 1968; Fanning and Pilson, 1973). Analytical precision is generally $\sim 3\text{-}5\%$ for all species, but ranges to $\sim 10\%$ for NH_4^+ in some samples taken in 1977 because of the short incubation times and correspondingly lower concentrations in those cases.

When more than two analyses were available for a core sample, fluxes were calculated by plotting the quantity $V_t(C_t - C_o)$ versus t where t = time of water sample removal from the core box, V_t = volume of water overlying the core at time t , C_t = concentration of solute at time t , and C_o = concentration at time of first sampling of the core or an arbitrary reference concentration such as bottom water. A linear increase in $V_t(C_t - C_o)$ generally occurred and the net flux was calculated by dividing the resulting slope of the least squares regression line by core surface area. Representative plots illustrating linearity for time dependent Mn^{++} and NH_4^+ concentration increases in water overlying box cores are given in Aller (1980a, b) and for $\text{Si}(\text{OH})_4$ in Figure 2. The flux was calculated in the same way when only two points were available but without a statistical determination of slope.

2. Results

Pore water $\text{Si}(\text{OH})_4$ profiles at FOAM, NWC, and DEEP for fall 1975 and winter-spring 1976 are given in Figure 3. Fall concentrations may be higher than *in situ* because samples were squeezed at room temperature (Fanning and Pilson, 1971).

The measured NH_4^+ , Mn^{++} , and $\text{Si}(\text{OH})_4$ fluxes for each station are listed in Table 1 along with date of collection, station depth, and temperature of collection

or incubation. NH_4^+ and Mn^{++} fluxes at FOAM, NWC, and DEEP are from Aller (1980a, b). The SACHEM NH_4^+ flux was measured in conjunction with J. Rosenfeld (1977); Mn^{++} at SACHEM has not been previously reported. Sandy cores from stations 1 and 2 developed small leaks for a short period and it is possible that the pore water profiles and thus fluxes were altered slightly as a result. Values for weight loss on ignition (475°C) and ^{232}Th concentrations in the top 0-1 cm of sediment at each station used later are from Aller, 1980a and Aller *et al.*, 1980 (SACHEM not previously reported).

3. Discussion

Seasonal variation. The flux of NH_4^+ , Mn^{++} , and $\text{Si}(\text{OH})_4$ from bottom sediments of Long Island Sound varied with both season of collection and depositional environment (Fig. 4). The general ranges of these fluxes are similar to those reported from other nearshore regions (Graham *et al.*, 1976; Eaton, 1979; Elderfield *et al.*, 1981 summary of Zeitzschel, 1980). Seasonal variation reflects predominately the temperature dependence of the particular dissolution reactions involved, transport mechanisms, and changes in the composition of organic source material through the year (Davies, 1975; Nixon *et al.*, 1976; Nixon *et al.*, 1980; Martens and Klump, 1980; Elderfield *et al.*, 1981).

Table 1. Direct net flux measurements.

Station	Date	Depth	T ($^\circ\text{C}$)	NH_4^+ (mmoles/ m^2/day)	Mn^{++} (mmoles/ m^2/day)	$\text{Si}(\text{OH})_4$ (mmoles/ m^2/day)
SACHEM	27 July 75	3	22.1	5.2	3.0	4.8
FOAM	8 July 75	7	22	2.2	0.67	4.3
FOAM	17 Nov 75	15	0.84	0.16	2.4	
FOAM	18 Mar 76	4	0.26	0.08	0.78	
NWC	16 July 75	14	22	3.2	3.7	10.6
NWC	29 Oct 75	15	2.2	3.5	7.5	
NWC	23 Mar 76	4	0.28	0.03	1.1	
DEEP	23 July 75	35	22	1.3	1.4	6.7
DEEP	12 Nov 75	15	0.33	0.097	1.7	
DEEP	13 Apr 76	4	0.19	0.013	0.8	
1	21 July 77	25	21	0.9, 0.09	-0.16, -0.20	1.0, 3.7
2	21 July 77	25	22	-1.0, -0.43	-0.28, -0.61	0, 2.4
3	23 July 77	14.6	19	6.0, 8.0	2.6, 4.0	16.4, 19.8
4	29 July 77	12.5	21	1.5, 3.5	0.24, 0.54	9.5, 12.1
5	29 July 77	24	—	1.0, 0.78	0.20, 0.98	8.0, 7.6
6	29 July 77	7.6	—	5.2, 6.2	2.0, 0.89	6.6, 7.2
7	1 Aug 77	30	21	2.2, 2.9	1.2, 2.6	8.7, 11.7
8	1 Aug 77	29	21.5	1.7, 2.1	1.2, 0.97	9.7, 11.7
9	3 Aug 77	23	19.3	4.2, 5.0	2.4, 2.9	7.8, 9.2
10	3 Aug 77	24.7	20.1	0.45, 0.44	-0.24, 0	9.3, 6.1

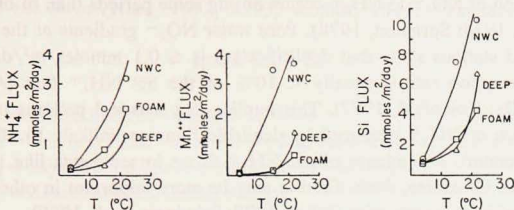


Figure 4. Net NH_4^+ , Mn^{2+} , and $\text{Si}(\text{OH})_4$ fluxes measured from sediments at FOAM, NWC, and DEEP as function of temperature. (NH_4^+ and Mn^{2+} data after Aller, 1980a, b).

The temperature dependence of a given solute flux can be quantified empirically in an 'apparent activation energy' obtained from the slope of a plot of $\ln(J)$ versus $1/gT$, where J = solute flux, g = gas constant, and T = absolute temperature. The apparent activation energy (E_a) so obtained can then be compared to the temperature dependence of factors which control the fluxes and possible dominance of a particular factor inferred. In the case of NH_4^+ , an E_a of 19 ± 3 Kcal/mole describes the NH_4^+ flux-temperature relationship and is nearly identical with the E_a of 18 ± 3 Kcal/mole found for the temperature dependence of microbial production of NH_4^+ in sediment at the same sites (Aller, 1980a; Aller and Yingt, 1980). This implies that production rate determines the basic seasonal release pattern, that consumption of NH_4^+ during nitrification must be a relatively constant proportion of the flux, and that N depletion of organic substrate may be balanced by supply. Because NH_4^+ production in pore water follows pseudo zero-order kinetics (Berner, 1974), transport processes such as biogenic reworking should not directly affect the temperature dependence of the flux at steady state (Billen, 1978; Aller, 1980c).

The predicted flux of NH_4^+ based on pore water gradients and production rate determination agree well with directly measured fluxes at the three stations (Aller, 1980a) and indicate that nitrification is unlikely to consume more than $\sim 20\%$ of the NH_4^+ released at any time. This percentage is consistent with data from similar muddy environments (Nixon *et al.*, 1976) although it can be higher, particularly in sands or sediments containing refractory or small amounts of organic material (Rowe *et al.*, 1975, 1977; Hartwig, 1976; Billen, 1978). The low percentage in this case is also consistent with agreement between E_a 's for NH_4^+ production and E_a 's for net NH_4^+ release in the central Sound. Because the proportion of the NH_4^+ flux which is oxidized may change seasonally in some sediments, the E_a 's for net NH_4^+ release could show corresponding variability between different sedimentary environments even if the E_a 's for NH_4^+ production rate within the deposits were the same.

Denitrification reactions could also influence the E_a of NH_4^+ fluxes if more com-

plete reduction of NO_3^- to NH_4^+ occurs during some periods than in others (Koike and Hattori, 1978; Sørensen, 1978). Pore water NO_3^- gradients at the three Long Island Sound stations show that denitrification is ≤ 0.1 mmoles/ m^2 /day and that NO_3^- consumption rate is usually $< 10\%$ of the net NH_4^+ flux (Aller, 1977, p. 325, 1980a; Rosenfeld, 1977). This implies that seasonal patterns of change in the proportion of NH_4^+ produced by denitrification are unlikely to affect the apparent temperature dependence of net NH_4^+ fluxes in sediments like those of the central Sound. Of course, denitrification may be more important in other regions of the Sound and in other estuaries (Billen, 1978; Seitzinger *et al.*, 1980).

Mn^{++} production rates are also controlled by organic matter decomposition but net Mn^{++} fluxes show a stronger and more variable temperature dependence than does NH_4^+ . Apparent activation energies of ~ 18 -46 Kcal/mole describe the net flux-temperature relation (Aller, 1980b). This variable dependence is presumably due to changing balances during the year between consumption and production reactions which together determine the net flux. For example, there is a seasonal oscillation in the depth of the oxidized sediment layer with the deepest visual oxidation during winter (Rhoads *et al.*, 1977). As a result, when Mn^{++} diffuses toward the sediment-water interface, oxic precipitation reactions occur over a smaller vertical sediment interval (~ 1 cm) during summer months than winter (~ 4 cm) so that a *proportionally* greater loss of Mn^{++} from solution by this means occurs during winter than summer. This loss accentuates and presumably causes variations in the observed temperature dependence of the net flux. In such a case, apparent activation energies cannot be related to any one set of temperature dependent processes and are subject to considerable uncertainty. Directly measured Mn^{++} fluxes do not agree as well as NH_4^+ fluxes with those predicted from pore water concentration gradients; however, agreement to within a factor of 2-3 is often obtained. Seasonal variation of both Mn^{++} and NH_4^+ fluxes and transport controls on fluxes are discussed in more detail elsewhere (Aller, 1980a, b).

$\text{Si}(\text{OH})_4$ release from sediments is due predominately to the dissolution of opaline silica formed by diatoms (Schink *et al.*, 1975). Like NH_4^+ and Mn^{++} , the net $\text{Si}(\text{OH})_4$ flux in the central Sound also varies seasonally in a regular fashion (Fig. 4). The apparent activation energies representing temperature dependence at each site are FOAM, 15.5; NWC, 21.1; and DEEP, 18.3 Kcal/mole. These are almost identical to the value of ~ 17 Kcal/mole reported by Kamatani and Riley (1979) for temperature dependence of initial dissolution rates of diatom frustules and freshly precipitated silica gel. Wollast (1974) also estimates a value of ~ 20 Kcal/mole. Aged silica gel or frustules can show a more variable temperature dependence of dissolution but lie between ~ 10 -25 Kcal/mole (see data of Kamatani and Riley, 1979).

The reason the Si fluxes show a similar temperature dependence to that of opaline silica dissolution can be seen as follows. Si dissolution rates can be described by

equations of the form (Hurd, 1972, 1973; Wollast, 1974; Kamatani and Riley, 1979):

$$R = k (C_b - C) \quad (1)$$

where:

R = production rate of dissolved silica

k = first order rate constant including the effect of surface area

C_b = asymptotic silica concentration or solubility

C = dissolved silica concentration.

Assuming the sediment pore water $\text{Si}(\text{OH})_4$ distribution which supports the flux represents a balance between diffusion and dissolution reactions only, that is that advective transport such as sedimentation is unimportant over the time scales of interest, then the steady state pore water $\text{Si}(\text{OH})_4$ concentration gradient is given by (e.g. Berner, 1980):

$$0 = D_s \frac{\partial^2 C}{\partial x^2} + R \quad (2)$$

where:

D_s = whole sediment diffusion coefficient, assumed constant with depth

x = space coordinate, measured positive into sediment, origin at interface

Fick's first law gives the diffusive flux of $\text{Si}(\text{OH})_4$ across the interface $x = 0$ as (Berner, 1980):

$$J_{\text{Si}} = \phi D_s \left(\frac{\partial C}{\partial x} \right)_{x=0} \quad (3)$$

where:

ϕ = sediment porosity.

If at $x = 0$, $C = C_T$, a constant overlying water Si concentration, and $x \rightarrow \infty$, $\partial C / \partial x = 0$, then equations (1), (2), and (3) give:

$$J_{\text{Si}} = \phi \sqrt{k D_s} (C_b - C_T) \quad (4)$$

Because the temperature dependence of D_s and C_b are relatively small (Li and Gregory, 1974; Kamatani and Riley, 1979; Table 2) compared with that of k , the dependence of Si flux on temperature is controlled predominately by reaction rather than transport terms. Bioturbation can affect the transport term and may alter the apparent temperature dependence of the $\text{Si}(\text{OH})_4$ flux if benthic populations or their activity vary greatly seasonally (Aller, 1980c).

The pore water gradients can be used together with Fick's first law to estimate the $\text{Si}(\text{OH})_4$ fluxes and check for consistency between pore water measurements and directly measured fluxes. It has been shown previously that both NH_4^+ and Mn^{++}

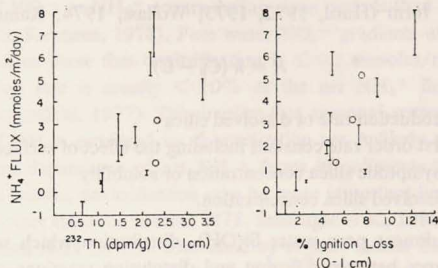


Figure 5. Net NH_4^+ flux (summer) at all stations compared with the quantity of fine-grained material, as assayed by ^{232}Th in the top 0-1 cm, or organic matter, as assayed by % weight loss on ignition. Stations SACHEM, FOAM, NWC, and DEEP (1975-76) plotted as open circles, stations 1 to 10 (1977) plotted as solid range bars.

net fluxes usually agree within a factor of 2-3 or better with those predicted from pore water gradients (Aller, 1980a, b). The $\text{Si}(\text{OH})_4$ flux is determined mostly by the concentration difference between the 0-1 cm sampling interval and overlying water. This gradient can be estimated in each case by assigning the average concentration over 0-1 cm to a depth 0.5 cm and assuming a linear concentration decrease to the overlying water value, C_T , represented by flux control-core water $\text{Si}(\text{OH})_4$ concentrations (Table 2).

$\text{Si}(\text{OH})_4$ diffusion coefficients in bulk sediment are estimated by modifying the diffusion coefficient in seawater by the factor ϕ^2 , where ϕ = sediment porosity (Lerman, 1978). This is equivalent to assuming a sediment formation factor $F \sim 1/\phi^3$ (see data of Krom and Berner, 1980; Andrews, 1980). The $\text{Si}(\text{OH})_4$ diffusion coefficient, D , in seawater at 25°C is 1.0×10^{-5} cm^2/sec (Wollast and Garrels,

Table 2. Calculated fluxes and reaction rate constants for reactive $\text{Si}(\text{OH})_4$.

Station	Date	C_T (μM)	C_{0-1}^{**} (μM)	C_b (μM)	ϕ^2	D_s (cm^2/day)	$(\partial C/\partial x)^\dagger$ ($\mu\text{M}/\text{cm}$)	J_{s1} ($\text{mmoles}/\text{m}^2/\text{day}$)	k ($1/\text{day}$)
FOAM*	5 Nov 1975	26.4	356	553	0.523	0.35	659	1.7	1.1
FOAM	18 Mar 1976	0.44	141	689	0.560	0.26	281	0.55	0.088
NWC	29 Oct 1975	15.5	302	539	0.697	0.46	573	2.2	6.4
NWC	23 Mar 1976	6.6	247	472	0.706	0.33	481	1.3	0.24
DEEP	12 Nov 1975	18.9	328	752	0.731	0.48	618	2.6	0.15
DEEP	13 Apr 1976	6.4	261	692	0.716	0.33	509	1.4	0.057

* The directly measured flux was obtained 17 Nov 1975 due to sample loss on 5 Nov 1975.

** Pore water Si concentration in 0-1 cm depth interval.

† gradient = $(C_T - C_{0-1})/(0.5)$.

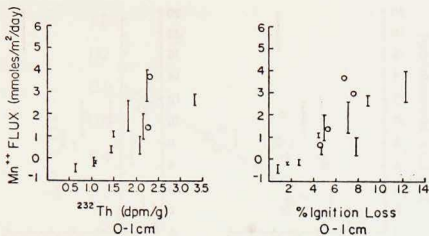


Figure 6. Net Mn^{++} flux (summer) at all stations compared with the quantity of fine-grained material, as assayed by ^{232}Th , or organic matter, as assayed by % weight loss on ignition. Symbols as in Figure 5.

1971). Using the Stokes-Einstein relation to correct for temperature (Li and Gregory, 1974), D is 0.54 and 0.76×10^{-5} cm^2/sec at $4^\circ C$ and $15^\circ C$ respectively. The appropriate value for ϕ^2 in the top 0-1 cm is calculated from % water contents (Aller, 1980a) and an assumed particle density of 2.5 g/cc . Bulk sediment diffusion coefficients, $D_s \sim \phi^2 D$ are given in Table 2 for each case.

The values of J_{Si} calculated from equation (3) are listed in Table 2. Excluding the fall NWC core, the ratios of directly measured flux (Table 1) to diffusion predicted flux (Table 2) average 1 ± 0.4 , indicating generally good correspondence between techniques. As always, this agreement may be fortuitous because of the many offsetting errors which cannot be explicitly evaluated, such as core warming, uncertainty in D_s , and heterogeneity of samples. An effect of biogenic reworking on $Si(OH)_4$ flux, particularly during the fall at NWC where the worst agreement is found (ratio of measured to observed is 3.4), could also be important in some cases.

Silica dissolution rates. Having demonstrated generally good agreement between measured fluxes and pore water profiles, it is possible to use equation (4) to estimate effective first order dissolution coefficients required to support the Si flux at each station. The values for D_s , C_T , and C_b used in calculation are listed in Table 2 and directly measured J_{Si} 's to which they are matched are in Table 1. C_b was estimated as the asymptotic concentration in each of the pore water profiles (Fig. 3) and does not necessarily represent an equilibrium saturation concentration (Schink *et al.*, 1975). Except for NWC fall data, the range of calculated k values, 0.06 - $1.1/day$, is comparable to those reported for dissolving diatom frustules at equivalent temperatures and also with k 's obtained from modeling sediment pore waters in other nearshore environments (Hurd, 1973; Vanderborcht *et al.*, 1977; Kamatani and Riley, 1979). The fall NWC k of $\sim 6.4/day$ is higher, but not excessively, than reported initial dissolution rate constants for relatively fragile diatoms. This discrepancy is presumably due to increased transport of $Si(OH)_4$ during biogenic re-

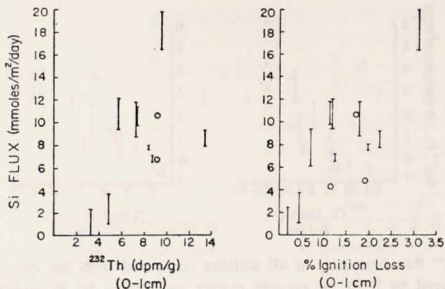


Figure 7. Net Si(OH)₄ flux (summer) at all stations compared with the quantity of fine-grained material, as assayed by ²³²Th, or organic matter, as assayed by % weight loss on ignition. Symbols as in Figure 5.

working not accounted for in the present calculation or to small scale patchiness in pore water and flux distributions. The NWC fall flux core was also consistently higher than expected with respect to the measured flux of NH₄⁺ and Mn⁺⁺ if average temperature dependences and pore water profiles are used for prediction (Fig. 4, Aller, 1980a, b).

Spatial patterns. In addition to a regular seasonal variation in fluxes there are general spatial trends in magnitudes of fluxes related to depositional environment. These are illustrated in Figures 5-7 where the summer ($T \sim 20-22^{\circ}\text{C}$) fluxes are plotted versus either the ²³²Th concentration or percent loss on ignition values in the top 0-1 cm of sediment at each station. ²³²Th reflects mineralogy, for example clay, and loss on ignition (LOI) is a rough measure of organic matter; both are inversely related to grain size. ²³²Th and LOI data are from Aller *et al.*, 1980, Aller, 1980a, or in the case of SACHEM, where only LOI is available, previously unpublished. Figures 5-7 demonstrate that there is a general increase in NH₄⁺, Mn⁺⁺, and Si(OH)₄ released from the seafloor as the quantity of small particles or organic material increases. A similar pattern has been inferred for NH₄⁺ fluxes from sediments of the North Sea (Billen, 1978). The bar lengths represent the range of flux magnitudes measured at each site during the 1977 survey. Low or negative fluxes may represent uptake in the overlying water column or increased relative importance of nitrification-denitrification within sandy, organic poor sediments (Billen, 1978).

These trends are consistent with the source reactions for each of the solutes. NH₄⁺ is a product of the biological remineralization of organic matter or of NO₃⁻ reduction (Koike and Hattori, 1978; Sørensen, 1978). The potential production of NH₄⁺ is therefore greatest and an anoxic environment most likely when organic matter is plentiful. Mn⁺⁺ is produced from dissolution of Mn-oxide coatings di-

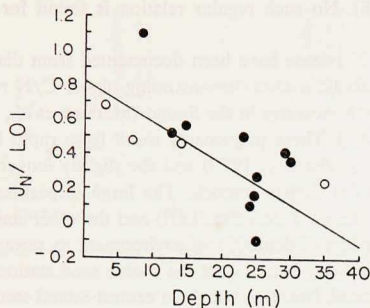


Figure 8. Relationship between ratio of the average summer NH_4^+ flux (J_N) to % weight loss on ignition (LOI) at a station and its water depth. Solid dots represent stations 1-10, open circles represent SACHEM, FOAM, NWC, and DEEP. The line corresponds to $y = -0.024x + 0.82$.

rectly or indirectly during anaerobic decomposition of organic matter (Froelich *et al.*, 1979). Mn-oxides are most abundant in fine-grained sediment with large specific surface areas as are the organic matter reductants which allow their dissolution.

Opaline Si and thus a source of dissolved $Si(OH)_4$ can be expected to covary to a certain extent as well with organic matter because of a common origin in diatoms. The few data for opaline Si from Long Island Sound (DeMaster, 1979) do show a trend (4 points) of increasing average Si (upper 1 m) with loss on ignition (0-1 cm). These same stations, however, do not show a simple relation between dissolved $Si(OH)_4$ release rates measured here and solid phase Si, presumably because of the large variation about the overall trend. The physical processes which concentrate small particles in certain regions of the estuary may also tend to accumulate diatom frustules in those same areas.

Although there are overall trends of increasing NH_4^+ , Mn^{++} , and $Si(OH)_4$ fluxes with decreasing average grain size there is considerable variability. Variation may be due to measurement error and the use of only two or three time series samples to estimate the flux or perhaps to patchiness of bioturbation, shown theoretically to be capable of increasing the flux of constituents like Si by factors of 2 to 5 (Aller, 1980c).

A portion of the scatter must also be due to the fact that the average grain size indicators do not always assay the quality or true proportion of reactive substrate at any site (Hargrave, 1973). For example, the NH_4^+ flux has a slight dependence on water depth in addition to grain size. A general trend of decreasing NH_4^+ release rates/organic matter content as station water depth increases can be shown by normalizing the NH_4^+ flux to loss on ignition (LOI) and plotting the resulting ratio

against depth (Fig. 8). No such regular relation is found for Mn^{++} or $Si(OH)_4$ fluxes.

Similar trends for N release have been documented from diagenetic modeling of pore waters and metabolic studies demonstrating higher C/N ratios in metabolized organic matter as depth increases in the Sound (Martens *et al.*, 1978; Aller, 1980a; Aller and Yingst, 1980). These presumably result from rapid loss of N relative to C during decomposition (Krause, 1959) and the slightly longer settlement time for planktonic debris at the deeper stations. The large disparities between station 3 (high flux/LOI) and station 2 (low flux/LOI) and the other stations may be caused by such local peculiarities of depositional environment as sewage input at station 3 and aerobic metabolism (nitrification) at the coarse sand station 2. Although NO_3^- fluxes were not measured, based on the three central Sound stations at which NO_3^- pore water gradients are known (Rosenfeld, 1977), it is unlikely that the NH_4^+ flux-depth relation simply reflects increasing nitrification with depth.

Reactive bottom regions. It was demonstrated in a previous paper that ^{234}Th ($t_{1/2} = 24.1$ days) produced during decay of ^{238}U in the water column of Long Island Sound tended to accumulate preferentially in fine grained deposits (Aller *et al.*, 1980). The quantity of this excess ^{234}Th in bottom sediments is a measure both of the extraction of refractory elements from the water column by particles and of short term particle transport or exchange between bottom regions. Figure 9 shows that, in general, bottom regions that release the greatest quantity of solutes to the water column are also most active in exchanging particles and extracting insoluble elements into sediments. The trend is least pronounced in the case of Si where stations 2 and 3 largely define the variation. As an example, areas of high dissolved Mn^{++} flux are likely to be the same regions where reprecipitated Mn-oxides scavenged from the water column accumulate, at least on ^{234}Th timescales. This suggests that such regions act as reflux-extractors for other elements associated with small particles or Mn, Fe-oxides (Evans *et al.*, 1977; Turekian, 1977). There are obvious exceptions, such as station 1, to the overall trend. In this case, sand ripple migration caused a build-up of excess ^{234}Th independent of factors that cause high solute fluxes.

The fine-grained regions of the estuary are therefore particularly reactive regions with respect to controlling water column composition and nutrient supply. Because of estuarine flow these muddy regions are situated away from the mouth (Meade, 1969). This means that the most intense recycling of material between sediment and overlying water takes place in the interior of the basin, accentuating the trapping characteristics of the estuary with respect to escape of material to the open shelf.

Role of benthic solute release in material balances. The seasonal and spatial patterns of benthic solute fluxes demonstrate that their relative importance in material

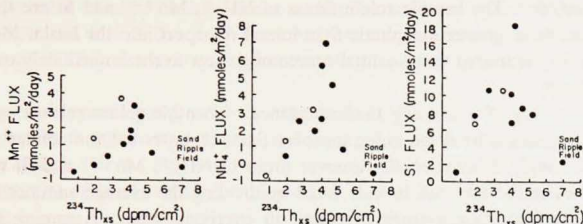


Figure 9. Correlations between average net solute release fluxes of Mn^{++} , NH_4^+ , and $Si(OH)_4$ and extraction of reactive elements as measured by the quantity of excess ^{234}Th at each station (^{234}Th after Aller *et al.*, 1980). Open circles are NWC and DEEP, solid dots are stations 1-10. High ^{234}Th at Station 1 is believed due to sand ripple migration.

cycles will vary with time and location. Localized importance is accentuated in Long Island Sound compared to other estuaries because 75% of fresh water runoff enters the basin east of $72^{\circ}30'W$ where its effect on solute supply is largely confined (Riley, 1956). The stations examined in the present study lie west of the region of major runoff.

There are several ways in which to place the importance of benthic fluxes in perspective. One crude way is to compare the average transport of water column solutes into the sampled area of the basin with that supplied from the bottom. The flux of water into the central Sound across a plane just east of stations 1 and 2 is $\sim 10^4$ m^3/sec (Riley, 1956; Gordon and Pilbeam, 1975; Wilson, 1976). The composition of this water is not well known but can be assumed to average $\sim 1 \mu M$ NH_4^+ , $0.04 \mu M$ Mn^{++} , and $3.6 \mu M$ $Si(OH)_4$ (Turekian, 1971; Bowman, 1977; Marine Sciences Research Center, 1978). Water transport into the western Sound across a plane just west of station 3 averages $\sim 10^3$ m^3/sec (Riley, 1956; Wilson, 1976), with a composition of $\sim 2 \mu M$ NH_4^+ , $0.04 \mu M$ Mn^{++} , and $\sim 14 \mu M$ $Si(OH)_4$ (Bowman, 1977, Marine Sciences Research Center, 1978). The area of the Sound lying between stations 1 and 2 in the east and station 3 in the west corresponds to $\sim 75\%$ of the total basinal area or $\sim 2.39 \times 10^9$ m^2 . This means that lateral transport can supply an areal average of ~ 0.43 , 0.015 , and 1.8 $mmoles/m^2/day$ of NH_4^+ , Mn^{++} , and $Si(OH)_4$ respectively to the central and western basins. Surface runoff from rivers such as the Housatonic in this region should represent a relatively small source (Riley, 1956, 1959).

In comparison, the average summer NH_4^+ , Mn^{++} , and Si fluxes for all 14 stations are 2.7 ± 2.2 , 1.4 ± 1.4 , and 7.9 ± 4.2 $mmoles/m^2/day$. If apparent activation energies of 19, 35, and 18 Kcal/mole for NH_4^+ , Mn^{++} , and Si fluxes are assumed, then the overall summer averages can be used to obtain the respective yearly averages (by integration of the Arrhenius equation) of ~ 1.2 , 0.42 , and 3.5

mmoles/m²/day. The benthic solute fluxes of NH₄⁺, Mn⁺⁺, and Si are therefore of comparable or greater magnitude than lateral transport into the basin. More importantly they represent the proximal source of solutes to the immediately overlying water column.

A second way of evaluating the importance of benthic solute release on water column processes is by determining turnover times of water column solutes relative to bottom supply. Characteristic turnover times of NH₄⁺, Mn⁺⁺, and Si with respect to bottom sources can be calculated by dividing the average summer benthic flux of each into their average inventory in overlying water. Assuming average summer concentrations of ~ 1 μM, 0.04 μM, and ~ 7 μM for NH₄⁺, Mn⁺⁺, and Si (after Turekian, 1971; Bowman, 1977; Marine Sciences Research Center, 1978) and a mean depth of ~ 20 m gives 7, 0.6, and 18 days respectively. The true turnover time for NH₄⁺ must be shorter than this because of additional major sources such as water column regeneration (Harris, 1959; Bowman, 1977). Note also that the value of ~ 0.6 days for Mn⁺⁺ is comparable to the residence time of < 1.4 days calculated for the reactive element ²³⁴Th (Aller and Cochran, 1976). These estimates are of course very approximate because the spatial and seasonal variability in both bottom solute flux and overlying water inventories require a corresponding local variability in turnover time for each element.

As in other nearshore environments (Davies, 1975; Rowe *et al.*, 1975, 1977; Nixon *et al.*, 1976; Billen, 1978), the supply of NH₄⁺ from bottom sediments is a major source of dissolved N for plankton. In Long Island Sound the average N requirement is 5-6 mmoles/m²/day (Harris, 1959). This means that 20-25% of this can be supplied on the average from the seafloor, assuming a yearly average flux of 1.2 mmoles/m²/day, and the remainder from regeneration in the water column. This percentage may be much higher or lower depending on location, season, and the importance of other bottom derived nitrogen species such as nitrate or dissolved organic nitrogen (Figs. 4, 5). Future studies on plankton productivity should be cognizant of the potential for spatial variability in nutrient supply from underlying sediments.

4. Conclusions

The flux of the solutes NH₄⁺, Mn⁺⁺, and Si(OH)₄ from bottom sediments to the overlying waters of Long Island Sound varies spatially and temporally in a regular fashion. Summer fluxes, representing the maximum values of the year, range from -1 to 8, -0.6 to 4, and 0 to 20 mmoles/m²/day for NH₄⁺, Mn⁺⁺, and Si(OH)₄ depending on location. Seasonal changes in flux from muds are related predominately to temperature sensitivity of dissolution or metabolic reactions in the sediment. The temperature dependence of NH₄⁺ and Si(OH)₄ fluxes are virtually identical to the apparent activation energies of ~ 19 and ~ 17 Kcal/mole which govern their production reactions. Because of non-conservative behavior

which probably changes in importance within the sediment from one time of the year to the next, Mn^{++} fluxes are more variably temperature dependent than either NH_4^+ and $Si(OH)_4$; an average apparent activation energy of ~ 35 Kcal/mole is found.

Large scale spatial patterns in the magnitude of summer solute fluxes are controlled by the distribution of fine-grained material and associated accumulation of organic matter. The net fluxes of NH_4^+ , Mn^{++} , and $Si(OH)_4$, all vary directly with the proportion of small particles or organic matter in surface sediment.

Bottom areas that are most active in releasing solutes into the water column are also most active in exchanging particles and extracting reactive elements into the bottom. This is shown by an overall direct correlation between magnitude of solute flux and ^{234}Th excess inventories. The muddy regions of the estuary are particularly reactive. Because of estuarine flow these reactive areas tend to be in the interior of the basin thereby accentuating the trapping nature of the environment.

The temperature corrected yearly average flux of NH_4^+ , Mn^{++} , and $Si(OH)_4$ from the bottom is comparable to or greater than the areal average flux to the basin due to lateral transport in the water column. The actual relative importance will vary with location and season. Characteristic turnover times of water column NH_4^+ , Mn^{++} , and $Si(OH)_4$ with respect to bottom supply are 7, 0.6, and 18 days, illustrating the importance of benthic fluxes to local water column composition.

Taken together these data are further evidence that direct inputs to the estuary are minor controls on reactive solute distribution relative to processing within the estuary.

Acknowledgments. Thanks go to fellow divers M. Pimer, "Kee" Muschenheim, and J. Yingst for aid in core retrieval. J. Boucher and W. Ullman provided lab assistance. This work was supported at various times by ERDA grant EY-76-S-02-3573 (to K. K. Turekian), NSF grant GA-42-838 (to D. C. Rhoads), the Louis B. Block Fund of the University of Chicago and NSF grant OCE-7900971 (to R. C. Aller).

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