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SEDIMENT-SEAWATER EXCHANGES OF NUTRIENTS AND TRANSITION METALS IN AN ALASKAN FJORD¹

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Resurrection Bay (southcentral Alaska) is a single silled fjord-estuary having a basin depth of 290 m (at Station RES 2.5) and a sill at approximately 185 m. The inner basin waters are renewed annually during May-October, but during the oceanographic winter period the basin waters remain relatively isolated from a downwelling flushing of bottom waters that occurs in the outer fjord as a result of a coastal convergence. The seasonal hydrography and dissolved oxygen distributions within this basin have been described by Heggie *et al.* (1977).

Figures 1 and 2 show pore water profiles for $\text{NO}_3\text{-N}$, $\text{NH}_3\text{-N}$, $\text{SiO}_4\text{-Si}$, $\text{PO}_4\text{-P}$, titration alkalinity and solid phase and soluble concentrations of the transition metals Fe, Mn, and Cu within the surface sediments of the fjord basin (Station RES 2.5; May 1975). There is no evidence for significant advective transport in these sediments so that the profile inflexions indicate zones of chemical reaction and transport of species in the pore water is predominantly *via* ionic diffusion. Table I gives species concentrations at the base of the water column and for interstitial water extracted from approximately the upper 5.5 cm of the sediment. The computed fluxes across the sediment-seawater interface are for ionic diffusion coefficients (D_a) assuming that the bottom water concentrations listed approximate those at the interface. In view of the large concentration differences involved this assumption is not believed to be a major source of error.

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Maximum nitrate (plus nitrite) concentrations over this period within the oxygenated sediment layer were in excess of $90 \mu \text{mole } \ell^{-1}$ (Fig. 1). In the absence of regeneration, surface porewater concentrations should approximate those measured in bottom waters following renewal periods ($\sim 30 \mu \text{mole } \ell^{-1}$). Nitrate produced by aerobic decomposition of biogenic material (C:N::106:15) can raise surface sediment porewaters only up to approximately $50 \mu \text{mole } \text{NO}_3\text{-N } \ell^{-1}$. Since the measured nitrate concentration of the surface interstitial water cannot be accounted for by standard regeneration stoichiometry it is suggested that the "excess" nitrate is due to nitrification at the boundary. Added evidence for such an ammonia oxidation hypothesis is supplied by the indicated gradients and computed benthic flux of this species. The ammonia concentration difference across the benthic boundary is in excess of two orders of magnitude (Table I; Fig. 1) and during 1973-75 ammonia concentrations at the bottom of the fjord basin at no time exceeded $1 \mu \text{mole } \ell^{-1}$ (although values $> 2 \mu \text{mole } \ell^{-1}$ were found 25 m above the boundary in January and April 1975; Heggie *et al.*, 1977). The computed benthic flux of $17.7 \mu \text{mole cm}^{-2} \text{ yr}^{-1}$ is capable of supporting a minimum gradient in ammonia of $1.6 \times 10^{-7} \mu \text{mole cm}^{-4}$ (from a mean turbulent diffusion coefficient of $3.5 \text{ cm}^2 \text{ sec}^{-1}$ computed for sill height). This would be equivalent to a concentration difference between the sediment interface and the top of the basin at sill height (approximately 100 m) of $1.6 \mu \text{mole } \ell^{-1}$; this latter has not been observed. Interstitial water ammonia increases linearly with depth to around 50 cm (Fig. 1). Diffusive transport along this gradient was computed at not less than $2.7 \mu \text{mole cm}^{-2} \text{ yr}^{-1}$; a flux which, at steady state, would be insufficient to maintain the estimated benthic boundary flux ($17.7 \mu \text{mole cm}^{-2} \text{ yr}^{-1}$) discussed above. It is concluded that these several observations require additional production of ammonia at the interface, part of which is oxidized to nitrate.

Dissolved oxygen concentrations in basin waters during 1973-75 decreased from around $180 \mu \text{mole } \ell^{-1}$ after replacement (October) to less than $50 \mu \text{mole } \ell^{-1}$ by the end of the winter (May). Mean annual consumption rates for the inner basin have been estimated at $165 \mu \text{mole } \ell^{-1} \text{ yr}^{-1}$, with consumption rates some 5 m above the sediment at approximately $250 \mu \text{mole } \ell^{-1} \text{ yr}^{-1}$. Assuming that interfacial oxygen concentrations approximate those measured at the base of the water column, the minimum (molecular) diffusive flux of oxygen into the sediment is calculated to vary seasonally between 22 and $5 \mu \text{mole cm}^{-2} \text{ yr}^{-1}$. A mass balance for $\text{NO}_3\text{-N}$ and $\text{NH}_3\text{-N}$ estimates that 50 percent of the oxygen consumed in the bottom water (5 m above the sediments) during the winter of 1974-75 may be due to ammonia oxidation. Annual net productivity over this period in Resurrection Bay has been estimated at $19 \text{ mole C m}^{-2} \text{ yr}^{-1}$ (Heggie *et al.*, 1977) some 30 percent of which ($\sim 6 \text{ mole C m}^{-2} \text{ yr}^{-1}$) may be accounted for using conventional organic matter oxidation stoichiometry by oxidation in deep and bottom waters, with less than an additional 1 percent oxidized in the surface oxic sediments.

Maximum pore water concentrations of manganese ($305 \mu \text{mole kg}^{-1}$) were found in the top 5.5 cm of sediments, decreasing to $50 \mu \text{mole kg}^{-1}$ at 14-22 cm depth, and thereafter remain relatively constant to the maximum depth sampled (130 cm; Fig. 2). Maximum solid phase concentrations (Fig. 2) occurred in the top 0.5 cm of sediment. These distributions are attributable to diagenetic reduction and mobilization below the redox boundary, with upward diffusion and reprecipitation in the oxic zone. Pore water contents of iron increase with depth to a maximum of around $390 \mu \text{mole kg}^{-1}$ over the 42-47 cm depth zone (Fig. 2). From this surface sediment gradient, an ionic diffusion flux of approximately $1.8 \mu \text{mole cm}^{-2} \text{ yr}^{-1}$ was computed, considerably larger than the estimated flux of $0.08 \mu \text{mole cm}^{-2} \text{ yr}^{-1}$ across the benthic boundary

(Table 1). It would appear that remobilized reduced iron is efficiently trapped in the surface sediments and that, unlike manganese in this environment, little escapes into the water column.

The depth distributions of the redox species O_2 , NO_3-N , Mn and Fe are consistent with a model of organic matter degradation in the sediments by oxidants in order of free energies made available to the organism. These oxidants are consumed in the top 5.5 cm of this fjord basin. The depth distribution of copper in Resurrection Bay sediments is shown in Figure 2. Heggie and Burrell (1979) have presented a model which incorporates remobilization in the surface sediments with a flux into the water column and a removal reaction in sub-surface sediments.

A relative measure of the remobility of these transition metals is given by normalizing the computed sediment-seawater flux to the apparent equilibrium solid phase concentration of each metal as shown in Table II. The relative remobilities are $Mn > Cu > Fe$. Table III summarizes the computed interface fluxes together with approximate standing stocks in the overlying water. The sub-sill basin water of Resurrection Bay is renewed annually (Heggie *et al.*, 1977): approximately 60 percent of the fjord water volume. If the time required to double the concentration of a species in the water column *via* input across the benthic boundary were of the same order as the residence time of the water then this transport could be an important component of the estuarine geochemical balance: this appears to be the case only for manganese in this environment. It is inferred that, for the other species considered here, riverine influx and regeneration in the water column are quantitatively more important processes.

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Table I

Benthic boundary species concentrations and fluxes

Species	C (μ mole ℓ^{-1})		$*D_a \times 10^{-6}$ ($\text{cm}^2 \text{sec}^{-1}$)	F (μ mole $\text{cm}^{-2} \text{yr}^{-1}$)
	B.W.	I.W.		
$\text{NO}_3\text{-N}$	36.5	91.7	11.6	7.0
$\text{NH}_3\text{-N}$	< 1.0	137.5	11.6	17.3
$\text{PO}_4\text{-P}$	2.6	17.2	8.0	1.3
$\text{SiO}_4\text{-Si}$	54.8	295.5	3.0	7.9
Mn	0.06	304.9	3.8	12.6
Fe	0.01	1.7	4.2	0.08
Cu	0.03	0.16	4.2	0.006

B.W. = bottom water

I.W. = surface ($\sim 0 - 5$ cm) interstitial water* Diffusion coefficients from Li and Gregory (1974) interpolated to 5°C .

Table II

Sediment - seawater flux of Mn, Fe, Cu
normalized to apparent equilibrium contents of
solid phases

Element	Flux (F)	Equil. solid	C/F
	$\text{mg cm}^{-2} \text{yr}^{-1}$	phase conc. (C) mg cm^{-2}	yrs
Mn	0.69	3.3	4.7
Cu	4×10^{-4}	0.2	500
Fe	4.5×10^{-3}	190	42,222

* Sediment density $2 \times 10^{-3} \text{ kg cm}^{-3}$; 5 cm sediment depth.

Table III

Benthic flux, standing crop estimates and doubling time.
Resurrection Bay 1974-75

Species	Annual Mean water column concs. μ mole ℓ^{-1}	Annual Mean Standing crop (C) μ mole cm^{-2}	Flux (F) μ mole $\text{cm}^{-2} \text{yr}^{-1}$	Doubling time (C/F) yrs
$\text{NO}_3 + \text{NH}_3$	20.	600	24.	25
SiO_4	36.7	1100	7.9	139
PO_4	1.9	56	1.3	43
Mn	0.013	0.37	12.6	0.03
Cu	0.008	0.23	0.006	38

Figure 1. Resurrection Bay pore water nutrient data May 1975.

Figure 2. Resurrection Bay pore water and solid phase transition metal data, May 1975.