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**Transport of Trace Metals
in Nearshore Sediments**

by

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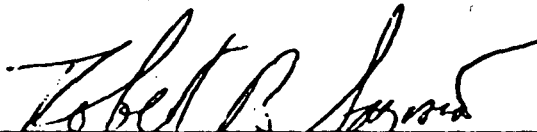
Doctoral Dissertation

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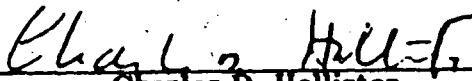
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ABSTRACT

The focus of this thesis is on rates of transport of metals both across the sediment/water interface and within the sediment column of nearshore sediments. The early diagenesis of several first-row transition metals exhibiting a variety of behaviors in the ocean -- Mn, Fe, Co, Ni, and Cu -- has been studied intensively at a site in Buzzards Bay, Mass. By limiting the study to a single site, independent measurements over the seasonal cycle of the concentrations of the metals in pore water, of the pore water constituents important to metal cycling, and of particle and solute transport rates could be made at the same site. In addition, a direct, in situ study of the interaction of chemical and transport processes was undertaken using radiotracer techniques. Thus, the study emphasizes the mechanisms of metal cycling near the interface of nearshore sediments.

Transport rates were estimated using excess ^{234}Th distributions for particle transport, and pore water ^{222}Rn deficit distributions for solute transport. Particle transport rates, modeled by analogy to Fickian diffusion, ranged from $7\text{--}80 \times 10^{-8}$ cm^2/sec , with excess ^{234}Th reaching to 2–2.5 cm below the interface. There was a significant seasonal variation in rates, with a warm-season average of 40×10^{-8} cm^2/sec and a cold-season average of 20×10^{-8} cm^2/sec . ^{234}Th -derived mixing rates were applied to Mn distributions through a mass balance model of Mn cycling. It was found that a particulate flux due to bioturbation, from the net dissolved Mn removal layer to a net dissolved Mn production layer adjacent to the interface, was as large as 38% of net dissolved Mn production. Mixing of particulate Fe sulfides may have a similar importance for Fe cycling.

Solute transport was estimated using measured $^{222}\text{Rn}/^{226}\text{Ra}$ disequilibrium. The pore water ^{222}Rn deficit could be explained using a model including vertical molecular diffusion and exchange with overlying seawater via exchange of pore water with bottom water in rapidly flushed burrows. Cores taken in all seasons could be split into three groups: (1) December through March: the ^{222}Rn deficit was explained by vertical molecular diffusion alone; (2) early summer (June): irrigation affected the ^{222}Rn profile to a depth of at least 20 cm; (3) late summer/fall: irrigation was still important near the interface, affecting ^{222}Rn profiles to depths of 10–12 cm. ^{222}Rn deficits were adequately explained by an exchange parameter (α) which decreased exponentially with depth below the interface, but not by a constant- α model. Previous studies have explained irrigation using a constant exchange parameter throughout the irrigated layer. For comparative purposes, an α averaged over the upper 20 cm of the sediment column was calculated at the Buzzards Bay site: the range of depth-averaged α values found, $4\text{--}12 \times 10^{-7}$ sec^{-1} , is in agreement with values reported previously for a variety of nearshore sediments, using pore water SiO_2 as a tracer, of

$1-20 \times 10^{-7} \text{ sec}^{-1}$. ^{222}Rn -derived irrigation rates were applied to pore water Mn and Fe distributions. It was estimated that irrigation may contribute 20-40% of the dissolved Mn flux across the interface and about 20% of the dissolved Fe flux.

Study of pore water metal chemistry at the Buzzards Bay site included measurements of pore water Mn and Fe during all seasons, and measurements of Co, Cu, and Ni in two cores: one under late winter conditions when the interface is most oxidizing; one when sulfate reduction was very important in the upper centimeter of the sediments. Fe regeneration sufficient to produce enrichments on water column particles was observed only during periods of summer and fall when the interface was reducing; otherwise, oxidation of Fe to insoluble Fe(III) limited Fe fluxes. Mn, Co, Cu, and Ni fluxes varied inversely to Fe fluxes; the primary control on fluxes of these elements was their limited solubility in reducing marine systems. The control was least important for Mn and Co; fluxes of Ni and Cu were significantly greater than zero only when sulfate reduction was unimportant in the upper centimeter of the sediment column. Fluxes of Mn were sufficient to affect the water column Mn distribution, with enrichments on water column particulates of up to 10,000 ppm inferred from calculated fluxes. Tentative estimates of the turnover time of dissolved Co, Cu, and Ni in the water column relative to the benthic flux indicated that the flux may be a significant contributor to the coastal Co cycle (turnover time = 1 yr), but is less likely to be important to Cu and Ni cycles (turnover times greater than 2 yrs).

In situ radiotracer migration experiments were carried out at the Buzzards Bay site. ^{54}Mn , ^{59}Fe , ^{60}Co , and ^{63}Ni were released into the sediments at depths ranging from 2.5 to 7 cm below the interface. The order of mobilities was $\text{Mn} \gg \text{Fe} > \text{Co}, \text{Ni}$, which is similar to the solubility trend for these metals in reducing marine systems. ^{63}Ni and ^{60}Co were essentially particle-bound in these experiments; apparent diffusion coefficients calculated from their dispersion rates agreed with particle mixing rates from excess ^{234}Th distributions. Solid:solution distribution coefficients were calculated from ^{54}Mn dispersion and found to agree with directly measured values. The coefficient was approximately 15 (dpm/gm solid \div dpm/gm pore water) in the upper 0.5 cm and below 5 cm, and 5-10 from 0.5 to 5 cm. Distribution coefficients for ^{59}Fe were approximately 120 below 0.5 cm. Although the trend of the distribution coefficients is clear, the quantitative results from these experiments are preliminary, in that the model used to explain metal ion dispersion, when applied to the nonreactive tracer, ^{36}Cl , could only explain a portion of the ^{36}Cl distribution. The agreement between calculated and directly measured ^{54}Mn distribution coefficients, as well as the way the distributions of tracers varied as a function of apparent diffusion coefficient and time, provides evidence in favor of the adequacy of the model used.