

Measurements of Dispersivity and Retardation Factors in Marine Sediments using tritiated calcium chloride solution and Radium-226

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INTRODUCTION

One of the most commonly applied environmental tracers is radium, with four naturally occurring radioisotopes, ^{223,224,226,228}Ra ($t_{1/2} = 11$ d, 3.6 d, 1620 y, 5.7 y). Radium is a ubiquitous alkaline earth metal found in the crystal lattice of most silicate and carbonate minerals as well as sorbed onto clays and Mn- and Fe-hydroxide sediment coatings. It is chemically non-conservative and must be well-characterized for the successful application of Ra mass balances in environmental systems. Nevertheless, its relative ease of measurement and its common occurrence in a variety of geologic environments makes Ra highly useful for studying water transport and circulation patterns, particularly if all sources and sinks are quantified.

Within freshwater-salt water mixing zones of coastal aquifers, or the subterranean estuary (Moore, 1999), the sorptive behavior of Ra is poorly defined and sediment Ra contributions to a budget are often considered negligible. Sediment composition and physical properties, redox conditions, and pore water ionic strength affect the sorptive behavior of radium. Poor quantification in turn affects the reliability of the mass balance calculations. This sorption behavior may also impede the consistency of ²²²Rn, a ²²⁶Ra daughter, as a geochemical tracer. Both the Ra quartet and ²²²Rn are used to evaluate groundwater inputs to coastal systems such as estuaries, wetlands, and continental shelf (e.g. Cable et al., 1996; Moore 1996; Krest et al. 2000; Martin et al, 2007). Numerous geochemical studies have previously recognized the release of radium from particles in estuarine environments (e.g. Li and Chan, 1979; Elsinger and Moore, 1984; Webster et al., 1994, 1995; Moore et al., 1995). In the subterranean estuary, Bokuniewicz et al. (2004) have shown salt penetration into seafloor sediments greatly affects the pore fluid composition. Such salt water penetration is temporally and spatially variable, thus altering the sorption capacity of sediments as pore water ionic strength fluctuates. We derive here the dispersivity of permeable marine sediments and evaluate effects of salinity on Ra sorption in these sediments. Breakthrough curves for ²²⁶Ra and tritiated CaCl₂ solution (conservative tracer) were produced to determine how strongly Ra transport behavior in coastal sediments is coupled to solution ionic strength.

MATERIALS AND METHODS

A series of sediment column experiments were designed by homogeneously packing 2.2-cm inside diameter columns with ²²⁶Ra impregnated, fine-medium quartz sands with less than 1% mud/organic matter (Fig. 1). Column length and volume were 36.8 cm and 95 cm³, respectively. Porosity (ϕ) ranged between 0.30 and 0.38. Permeable marine sediments were soaked for two weeks in ²²⁶Ra-spiked deionized water, dried, and counted via gamma-ray spectrometry prior to packing. After packing the columns, they were capped, oriented vertically on a stand with the inlet at the bottom, and flushed with deionized water (using a HPLC pump) against gravity for 2 to 3 days to ensure full saturation and to remove highly

soluble Ra-salts precipitated during drying. During the experiments, tritiated (2200 dpm L⁻¹) solutions of 0.01 M CaCl₂ of varying salinities (0, 9, and 18) were passed through the sediment column at a constant flow rate. Column effluent was collected continuously every two minutes for the duration of the experiment using a fraction collector. Effluent samples were counted via liquid scintillation (Perkin Elmer Tri-Carb 3100TR) for the simultaneous determination of ³H and ²²⁶Ra (from ingrowth of ²²²Rn).

CXTFIT (Toride et al., 1995) was used to evaluate longitudinal dispersion from tritium breakthrough curves and subsequently retardation factors for radium. Assuming a linear sorption behavior, the partitioning coefficient (K_d) for radium in these permeable marine sediments was calculated from the retardation factor: $r_f = 1 + \frac{B_d}{\phi} K_d$ where B_d is the bulk density of the material (Fetter, 1999).

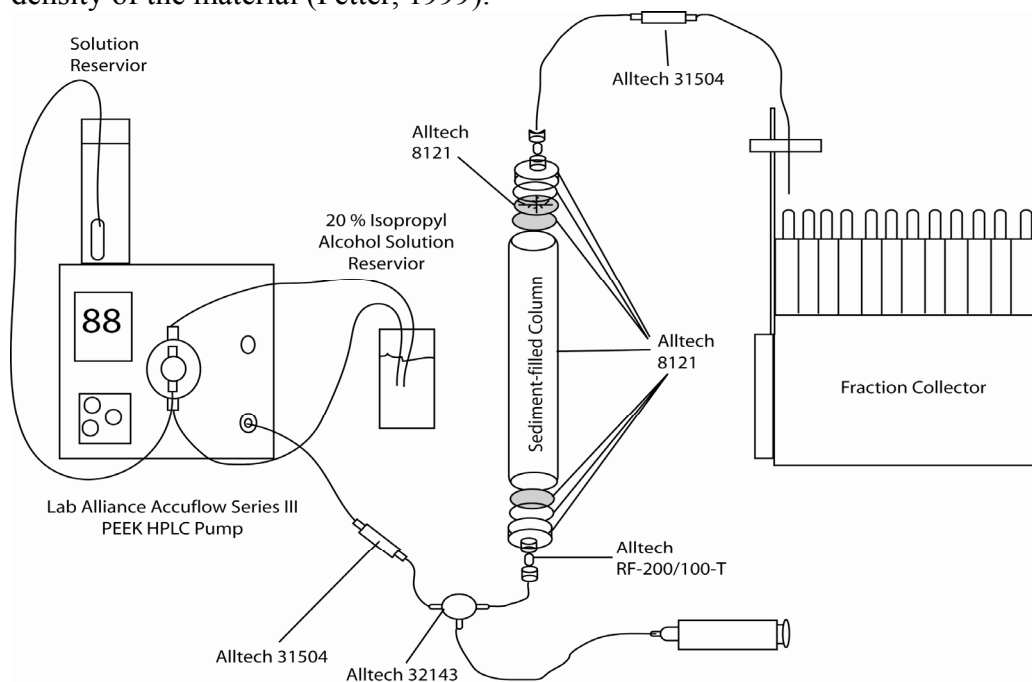


Figure 1. Sediment column flow-through system used to obtain ³H₂O and ²²⁶Ra breakthrough curves.

RESULTS AND CONCLUSIONS

Partitioning of radium between the aqueous and solid phases can be controlled by a number of processes, including sediment physical properties (e.g. Webster et al., 1995; Krest and Harvey, 2003), pore water pH and/or ionic strength (e.g. Li and Chan, 1979; Webster et al., 1995) and sulfate, manganese, or iron cycling in the subsurface environment. We test here only ionic strength. Breakthrough curves yielded no quantifiable response for radium desorption at 0 and 9 salinities (Fig. 2). Retardation factors for radium at salinity of 18 were estimated using two sorption models, local equilibrium and two-site kinetic sorption. The retardation factor (r_f) from the local equilibrium sorption model was approximately 1.85, while the two-site kinetic model was approximately 25% greater. The distribution coefficient, K_d , for radium based on this retardation factor found in the column experiments is about 0.15 to 0.19 cm³g⁻¹. These experiments suggest Ra sources from sediments are closely coupled to the pore fluid salinity and may have less to do with fresh groundwater sources than previously understood. In other words, in fresher nearshore coastal pore waters, radium occurrence may be associated with an incoming aquifer signal, while beyond the seepage face, pore water radium concentrations are more likely responding to salt water infiltration of sediments. In a

water column mass balance, these radium signals will be indistinguishable unless the sorption behavior is characterized.

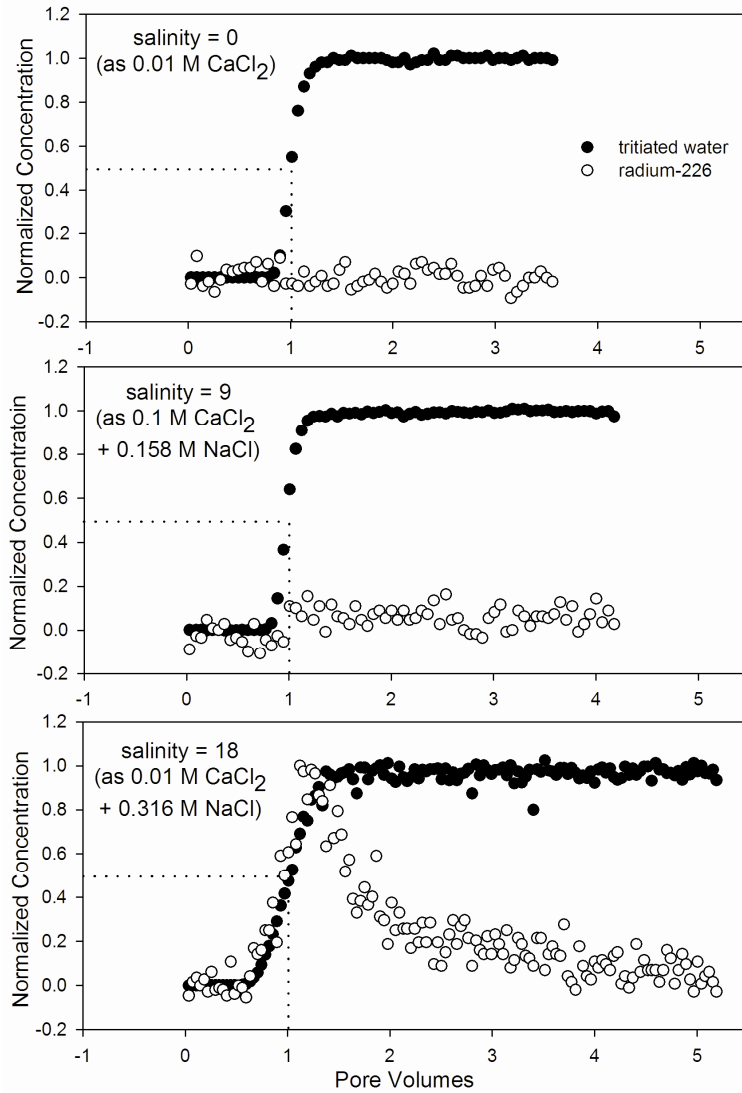


Figure 2. Breakthrough curves for $^3\text{H}_2\text{O}$ and ^{226}Ra at salinities of 0, 9, and 18.

Our column investigations of tritiated CaCl_2 solution yielded dispersivity estimates on the order of 1.03 to 5.96×10^{-3} m for scale length of 0.37 m (Table 1). Local variations in the flow field for permeable marine sands, on the scale of this column experiment, were minimal. Schulze-Makuch (2005) summarized field and laboratory longitudinal dispersivity studies and found a slope of 0.81 (i.e. the scaling exponent, m) for unconsolidated sediments. Our dispersivity values fall within the lower end of this data set and are consistent with other similar scale experiments.

Table 1: Dispersion results from breakthrough curves of tritiated CaCl_2 solution in unconsolidated sands.

Parameter (scale length = 0.368 m)	Salinity = 0	Salinity = 9	Salinity = 18
Hydrodynamic dispersion coefficient ($\text{cm}^2\text{sec}^{-1}$)	1.18×10^{-3}	1.42×10^{-3}	8.64×10^{-3}
Pore fluid velocity (cmsec^{-1})	0.0114	0.0114	0.0145
Longitudinal dispersivity (m)	1.03×10^{-3}	1.24×10^{-3}	5.96×10^{-3}

In conclusion, local flow field variations were not significant for this experiment. Radium desorption is strongest in the mid-salinity range of about 18. Isotherm batch studies covering more salinity regimes are being conducted to better characterize if K_d will change with ionic strength in these permeable marine sands.

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