Radioprotection, vol. **44**, n° 5 (2009) 185–190

DOI: 10.1051/radiopro/20095038

Dispersivity and distribution coefficients in marine sediments using ^{3}H and ^{226}Ra

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Abstract. Continental aquifers flow along topographic gradients toward coastlines in many geologic environments. Wherever aquifers intersect coastlines, ground water mixes with seawater infiltrated in marine sediments. In this mixing zone, sediment-pore fluid interactions create geochemical gradients that migrate back and forth on short (e.g., tides, waves) and long time scales (e.g. seasonal and eustatic sea level fluctuations). We focus on sorption and ion exchange characteristics of radium in these mixing zone sediments using laboratory column experiments. Previous studies have shown salinity affects radium sorption, but this process has not been investigated in porous sediments where solution ionic strength may fluctuate over a range of time scales. Additionally, different sediment types present within this subsurface zone may act as temporally and spatially variable source/sink sites for Ra. These sediments may have been underestimated in Ra mass balances for estimating coastal ground water fluxes. We performed microcosm sediment column experiments to examine Ra behavior and quantify the source/sink capacity of sediments. Longitudinal dispersivity results indicate local flow field variability was minimal during experiments. Radium desorption from sediments occurs rapidly (within 60 to 120 minutes) with exposure to solution and is generally high in the shallow portion of the subterranean mixing zone.

1. 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. In natural waters radium is non-conservative and may be sorbed to reactive sites or present as a dissolved ion in the 2+ valence state. It is chemically non-conservative and must be well-characterized for the successful application of Ra mass balances in environmental systems. Previous geochemical studies have recognized the release of radium from particles in surface water environments [1–4]. Distribution coefficients, K_d, have been measured for radium isotopes in marine beach sands ($K_d = 1.6$ to $5.6\,\text{cm}^3 \cdot \text{g}^{-1}$ [5]), freshwater peat sediments ($K_d = 144$ to $250\,\text{cm}^3 \cdot \text{g}^{-1}$ [6]), coastal bay sediments ($K_d = 210$ to $475\,\text{cm}^3 \cdot \text{g}^{-1}$ [7]), and aquifer sediments ($K_d = 50$ to $5000\,\text{cm}^3 \cdot \text{g}^{-1}$ [8]). It was generally determined that sediment desorption varied depending upon the Ra isotope of interest and a variety of geochemical conditions. 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 in the open ocean and if all sources and sinks are quantified.

Within freshwater-salt water mixing zones of coastal aquifers, or the subterranean estuary [9], where salinities may vary over time scales of hours to months and with depth in the sediments, the sorptive behavior of Ra is poorly defined. Salt penetration into seafloor sediments greatly affects the pore fluid composition [15, 16]. Such salt water penetration is temporally and spatially variable, thus potentially altering the sorption capacity of sediments as pore water ionic strength fluctuates. Sediment type and composition, sediment physical properties, pore water redox conditions and pH, and pore water ionic strength affect the sorptive behavior of radium. Despite these uncertainties, sediment Ra contributions to a geochemical mass balance calculations are often considered negligible. However, this sorption behavior may also influence the consistency of ^{222}Rn, a ^{226}Ra daughter, as a geochemical tracer, since radon production in the sediments is controlled by the presence of radium. Nonetheless both the Ra quartet and ^{222}Rn are used to evaluate groundwater inputs to coastal systems such as estuaries, wetlands, and continental shelf [10–14].

We derive here the dispersivity of permeable marine sediments and evaluate effects of salinity on Ra sorption in marine sediments. Breakthrough curves for ^{226}Ra and tritiated $CaCl_2$ solution (conservative tracer) were produced to determine how strongly Ra transport behavior in coastal sediments is coupled to solution ionic strength in subterranean estuary sediments. Laboratory results are compared to field measurements.

2. MATERIALS AND METHODS

A series of sediment column experiments were designed using permeable marine sediments obtained from a subterranean estuary in Florida, USA [13, 17]. Marine sediments were composed of fine-medium quartz sands with less than 1% mud and organic matter. Initially, sediments were soaked for two weeks in ^{226}Ra-spiked deionized water, after which they were dried. Sediments were immediately counted via gamma-ray spectrometry (2.01 ± 0.28 dpm g^{-1}, n = 3) and again after rinsing the sediments three times with deionized water (1.97 ± 0.32 dpm g^{-1}, n = 3). No statistical difference appears between these pre- and post-rinse sediments.

Column experiments were prepared by homogenously packing 2.2-cm inside diameter acrylic columns with the ^{226}Ra impregnated material (Fig. 1). Column length and volume were 36.8 cm and 95 cm^3, respectively. Sediment porosity (ϕ) ranged between 0.30 and 0.38 after packing columns. The columns were capped and oriented vertically on a stand with the inlet at the bottom. Deionized water was flushed through each experimental column using a low pressure HPLC-style pump against gravity for 2 to 3 days to ensure full saturation and to remove any highly soluble Ra-salts that may have precipitated during drying. During the experiments, tritiated (2200 dpm L^{-1}) solutions of 0.01 M $CaCl_2$ 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 ^{3}H and ^{226}Ra (from ingrowth of ^{222}Rn).

The transport code CXTFIT [18] 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, and the bulk density, B_d, of the material [19]:

$$r_f = 1 + \frac{B_d}{\varphi} K_d. \tag{1}$$

3. RESULTS AND CONCLUSIONS

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 (Fig. 2, Table 1). Local variations in the flow field for permeable marine sands, on the scale of this column experiment, were minimal. Schulze-Makuch [20] summarized field and laboratory longitudinal dispersivity studies and found a slope of 0.81 (i.e. the

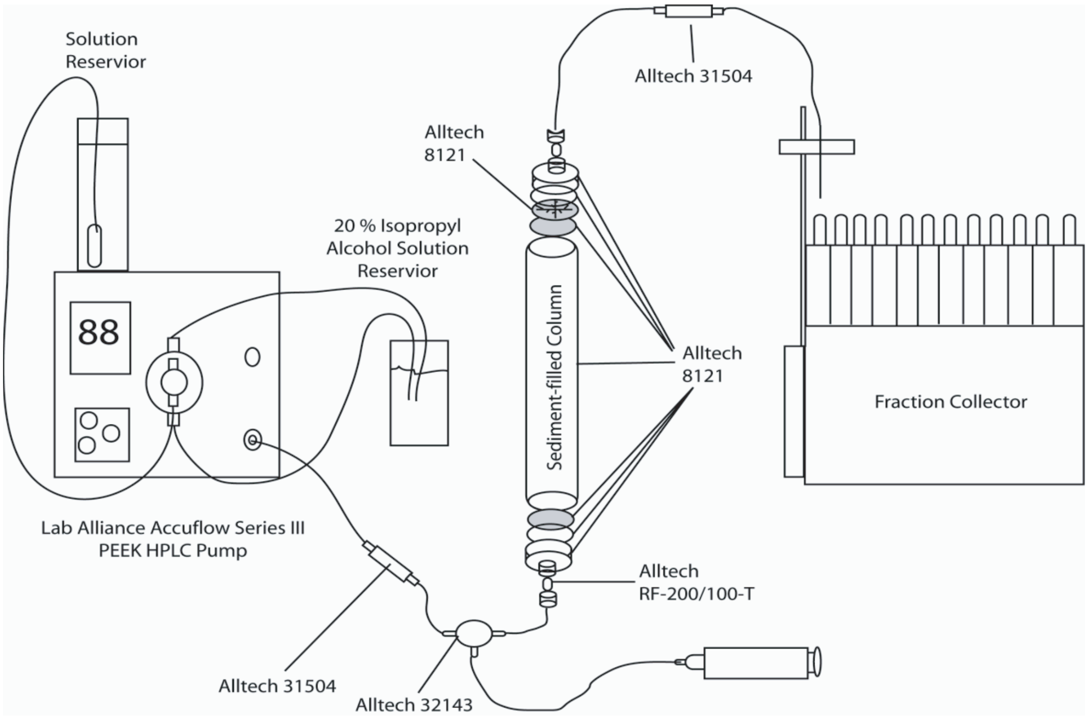

Figure 1. Sediment column flow-through system used to obtain ^{3}H and ^{226}Ra breakthrough curves.

scaling exponent, m) for unconsolidated sediments. Our dispersivity values fall within the lower end of these data [20] and are consistent with other similar scale experiments.

Partitioning of radium between the aqueous and solid phases can be controlled by a number of processes, including sediment physical properties [4, 6], pore water pH and/or ionic strength [1, 4], and sulfate, manganese, or iron cycling [7, 17, 21] in the subsurface environment. We test here ionic strength. Breakthrough curves yielded no quantifiable response for radium desorption at 0 and 9 salinities (Fig. 2). Retardation factors for radium at a salinity of 18 were estimated using two sorption models, local equilibrium sorption 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 $\mathrm{cm}^3 \cdot \mathrm{g}^{-1}$. These values most closely resemble K_ds found for marine beach sands [5].

These experiments demonstrate ^{226}Ra sources from sediments are closely coupled to the pore fluid salinity and two primary cases for the interaction between radium and sediments may be present. In fresher nearshore coastal pore waters, where the continental aquifers intersect coastal waters and the subterranean estuary is formed, radium is present from multiple sources. Radium occurrence nearshore may be associated with a discharging aquifer signal, as well as associated with sediment sources from matrix bound and sorbed sites. Fresh water carrying a radium signal may encounter Fe and Mn (hydr)oxides in the sediments. These Fe and Mn rich sediments may sorb the Ra and inhibit Ra contributions to the water column [7, 21]. In this case, it is possible that fresh groundwater sources quantified using Ra as a tracer may be underestimated within the seepage face.

When in situ measurements of dissolved ^{226}Ra in pore water are compared to sediment bound ^{226}Ra along a freshwater-seawater mixing zone in coastal sediments, we can calculate a distribution

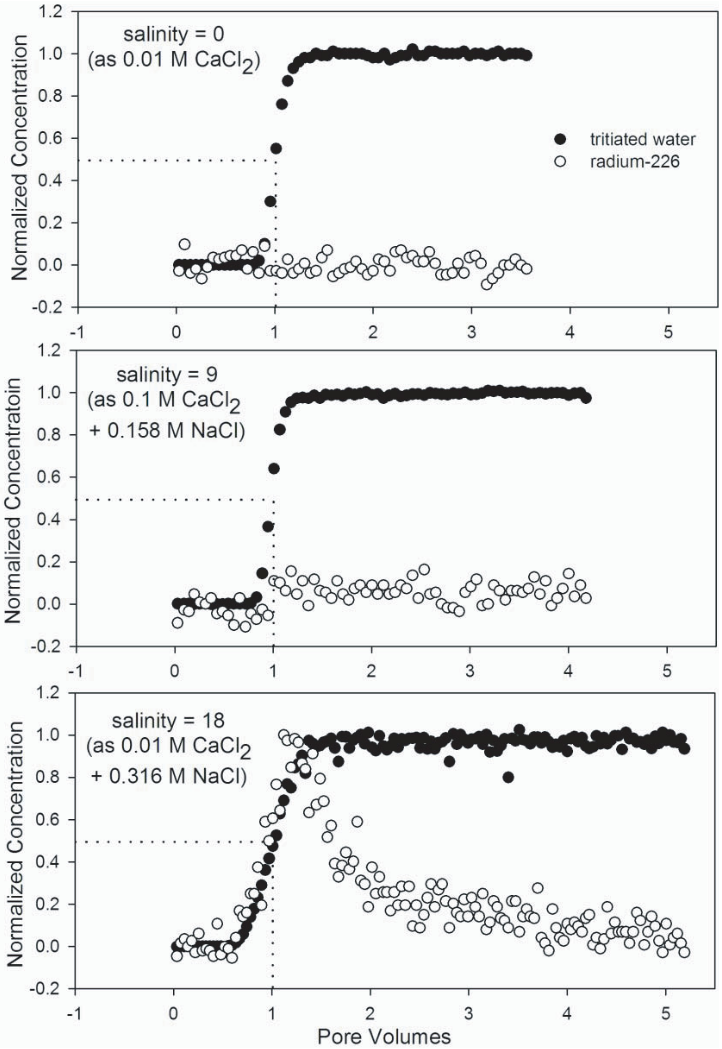

Figure 2. Breakthrough curves for ^3H_2O and ^{226}Ra at salinities of 0, 9, and 18.

coefficient directly from field measurements (Fig. 3). We find that over a wide range of salinities from about 0 to 23, K_ds are generally less than 50 cm^3 g^{-1}. However, for fresh groundwater within the seepage face plume, the ^{226}Ra distribution coefficients vary from 5 to 296 cm$^3 \cdot$ g^{-1}.

Beyond the freshwater seepage face and subterranean estuary, benthic radium sources may have less to do with groundwater aquifer sources than previously understood. Offshore, aquifer sources for Ra diminish and pore water radium concentrations are increasingly responding to sediment interactions

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 (cm^2 sec^{-1})	1.18×10^{-3}	1.42×10^{-3}	8.64×10^{-3}
Pore fluid velocity (cm sec^{-1})	0.0114	0.0114	0.0145
Longitudinal dispersivity (m)	1.03×10^{-3}	1.24×10^{-3}	5.96×10^{-3}

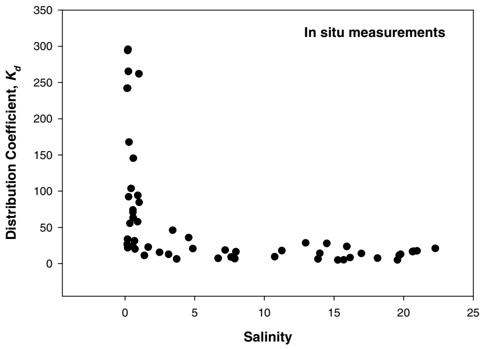

Figure 3. In situ K_d measurements for ^{226}Ra as determined from dissolved pore water and sediment emanation activities.

with salt water infiltration and resulting geochemical changes. In the subterranean estuary, several studies have shown salt penetration into seafloor sediments changes the pore fluid composition [15, 16]. Bokuneiwicz et al. [15] attribute much of this affect to salt dispersion in the pore waters. Pore water exchange in shallow sediments occurs almost anywhere that moving water is in contact with a sediment surface. Common processes creating this exchange may be physical (e.g. current movement over ripples, wave and tidal motion) or biological (e.g. bioirrigation, bioturbation) in origin. The net result is similar: rapid exchange of surface water with pore fluids can occur from 10 to 150 cm below the sediment-water interface (cmbsf), depending upon the magnitude of physical motion or biological activity [22].

Sediment column experiments, such as performed here, demonstrate that a rapid desorption of Ra from sediments will occur as surface water and pore water move through and exchange in the sediments. Additionally, the shallow exchange processes (less than 30 cmbsf) which are most prevalent on the seafloor may create an upper deficiency zone in the sediments relative to Ra. At offshore sites beyond the aquifer's hydrologic influence, bioirrigation and other pore water exchange processes may maintain low Ra presence in the porewaters and sediments, depending upon the sediment composition, due to the increased salinities and higher pH of pore waters [16, 17]. Radium fluxes to the water column in this zone beyond the seepage face and subterranean estuary more likely represent the magnitude of pore water exchange and would overestimate groundwater sources to the coastal waters. In a water column mass balance, radium signals of terrestrial submarine groundwater and recirculated seawater will be indistinguishable unless the desorption behavior and potential magnitude of sediment sources are characterized.

In conclusion, local flow field variations within the sediment columns were not significant for this experiment. Radium desorption is strongest in the mid-salinity range of about 18, which is representative of subterranean estuary conditions. Isotherm batch studies covering more salinity regimes are being conducted to investigate if K_d will change with ionic strength in these permeable marine sands. As we investigate these relationships we note that in nearshore sites where fresh groundwater is discharging to coastal waters, Ra sorption behavior may yield underestimates of groundwater flow, while in offshore sites where salt water penetration of sediments dominates, Ra desorption processes likely represent pore water exchange.

Acknowledgments

The U.S. National Science Foundation EAR#0403515 and the Louisiana State University Faulty Research Grant Program ORED#169509103 funded this research. The views expressed here are those of the authors and do not reflect the views of NSF. We thank Julia Wheatley for her assistance in the laboratory.

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