SECTION 1: INTRODUCTION AND BACKGROUND

Since the advent of the nuclear age, the fate of anthropogenic and naturally generated radioactive isotopes in the environment has been a major focus of groundwater transport studies. These radioactive isotopes can present a significant human and environmental health hazard, but also have already provided unique tracers for a variety environmental processes. For example, vertical groundwater movement has been traced using radioactive isotopes generated from atmospheric bomb testing [1] and iodine isotope changes in local environments have been correlated with nuclear accidents such as the one at Fukushima [2]. Historically, radium was used as a phosphorescent compound, but it currently only presents a natural radioactive health hazard. Radium at secular equilibrium can be liberated from deep formation waters during deep surface activities. Hydraulic fracturing in particular has recently raised some concerns due to the elevated presence of radium in produced waters, with concentrations in excess of 120 Bq/L [3]. In other situations, radium poses a risk as the source of cancer causing radon, which can accumulate in poorly ventilated basements [4]. Shales that are prime targets for hydraulic fracturing often experience significant changes in solution chemistry, particularly with respect to redox condition. Proper prediction of radium transport in these groundwater settings is a crucial component of mitigating the environmental risks associated with radium.

In parallel, the radium isotopes also have been leveraged as naturally occurring environmental tracers. The primary example uses a mass balance of radium isotopes in estuarine and near shore systems to provide estimates of subterranean groundwater discharge (SGD). The method constructs a simple conservative mixing model of local groundwater containing naturally occurring radium isotopes to reach a desired off shore end member [5]. While many of the predictions of this model have matched well with other methods, it is not able to resolve groundwater behavior within the estuarine systems, especially given that it is well understood radium isotopes are retarded by the presence of iron and manganese oxides [6]. This is complicated by the highly transient nature of these systems, which experience rapid changes in solution salinity, pH, and redox state. Development of more complete models of radium transport may unlock more detailed tracer capacities for naturally generated radium.

Radium isotope transport is dominated by advection and diffusion, where specific mineral phases, particularly iron and manganese oxides, preferentially retain radium isotopes. Solution behavior is limited to the limited formation of carbonate and sulfate complexes over most environmental pHs, with free radium remaining the dominant solution species [CITATION->CHIMIE DATABASE]. Previous work focused on sorption by measuring partition coefficients, Kd [CITATION->OLD PAPER???]. While a useful indicator for the extent of radium retention, these coefficients are primarily empirical and are not easily adapted to systems where conditions can change. A compilation of radium isotope Kd values saw significant variations in Kd for similar systems, even when only a synthetic iron oxide was considered [7]. Another study saw marked decrease in radium retention when ionic strength increased [MORE FIGURE]. [DISCUSS OTHER SOURCES] Ultimately, knowledge of radium solution behavior is fairly limited compared to other elements such as strontium or even barium, and there is little mechanistic understanding of processes controlling radium retention. PERHAPS DISCUSS HOW BARIUM IS USED AS AN ANALOG INCORRECTLY

Surface complexation modelling can help clarify behavior that may otherwise seem puzzling at first glance. A recent work examined the sorption of radium onto ferrihydrite and goethite, proposing a tetradentate reaction as the dominant mechanism [8].

MAYBE DISCUSS BARIUM AS ANALOG???? (NOT WORTH).

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