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 (Solomon, Poreda, Schiff, & Cherry, 1992) and iodine isotope changes in local environments have been correlated with nuclear accidents such as the one at Fukushima (Landis et al., 2012). Radium was used as a phosphorescent compound historically, but sees little, if any industrial use today, instead posing a natural radiological hazard. As an example, radium at secular equilibrium can be liberated from deep formation waters by anthropogenic or natural processes, posing both a direct and indirect hazard. 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 (Barbot, Vidic, Gregory, & Vidic, 2013). In other situations, radium poses a risk as the source of cancer causing radon, which can accumulate in poorly ventilated basements (Nazaroff, 1992). Experimental work studying radium transport can be used to build groundwater transport models that then inform policy decisions surrounding these scenarios.

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 (Moore, 2003). 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 (Gonneea, Morris, Dulaiova, & Charette, 2008). This is complicated by the highly transient nature of these systems, which experience rapid changes in solution salinity, pH, and redox state. Aside from a natural groundwater tracer, radium has also been identified as a possible marker for historic spills associated with hydrocarbon extraction (Lauer & Vengosh, 2016). This is possible because the radium isotopic signature of many shales differs significantly from that of local shallow groundwater (Warner, Christie, Jackson, & Vengosh, 2013). Making full use radium as a tracer requires, however, a careful accounting of the critical processes controlling transport.

Radium isotope transport is dominated by advection and diffusion, where specific mineral phases, particularly iron and manganese oxides, preferentially retain radium isotopes. Radium weakly forms complexes with carbonate and sulfate at pH values greater than 9, but is primarily free radium for most environmental conditions (Grivé, Duro, Colàs, & Giffaut, 2015). [PERHAPS A PHASE DIAGRAM?] Previous work has focused on sorption by measuring and comparing distribution coefficients, Kd (Bassot, Stammose, & Benitah, 2005; Beneš, Strejc, Lukavec, & Borovec, 1984). While a useful indicator for the extent of radium retention in a given system, these coefficients are primarily empirical and are not easily adapted to systems where conditions can change, as is typical of many groundwater systems. A compilation of radium isotope Kd values saw significant variations in Kd for similar systems, even when only a synthetic iron oxide was considered (Beck & Cochran, 2013).

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 (Sajih et al., 2014).

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

Barbot, E., Vidic, N. S., Gregory, K. B., & Vidic, R. D. (2013). Spatial and temporal correlation of water quality parameters of produced waters from devonian-age shale following hydraulic fracturing. *Environmental Science & Technology*, *47*(6), 2562–9. doi:10.1021/es304638h

Bassot, S., Stammose, D., & Benitah, S. (2005). Radium behaviour during ferric oxi-hydroxides ageing. *Radioprotection*, *40*, S277–S283. doi:10.1051/radiopro:2005s1-042

Beck, A. J., & Cochran, M. a. (2013). Controls on solid-solution partitioning of radium in saturated marine sands. *Marine Chemistry*, *156*, 38–48. doi:10.1016/j.marchem.2013.01.008

Beneš, P., Strejc, P., Lukavec, Z., & Borovec, Z. (1984). Interaction of radium with freshwater sediments and their mineral components. I. *Journal of Radioanalytical and Nuclear Chemistry Articles*, *82*(2), 275–285. doi:10.1007/BF02037050

Gonneea, M. E., Morris, P. J., Dulaiova, H., & Charette, M. a. (2008). New perspectives on radium behavior within a subterranean estuary. *Marine Chemistry*, *109*(3-4), 250–267. doi:10.1016/j.marchem.2007.12.002

Grivé, M., Duro, L., Colàs, E., & Giffaut, E. (2015). Thermodynamic data selection applied to radionuclides and chemotoxic elements: An overview of the ThermoChimie-TDB. *Applied Geochemistry*, *55*, 85–94. doi:10.1016/j.apgeochem.2014.12.017

Landis, J. D., Hamm, N. T., Renshaw, C. E., Dade, W. B., Magilligan, F. J., & Gartner, J. D. (2012). Surficial redistribution of fallout 131iodine in a small temperate catchment. *Proceedings of the National Academy of Sciences of the United States of America*, *109*(11), 4064–9. doi:10.1073/pnas.1118665109

Lauer, N., & Vengosh, A. (2016). Age Dating Oil and Gas Wastewater Spills Using Radium Isotopes and Their Decay Products in Impacted Soil and Sediment. *Environmental Science & Technology Letters*, acs.estlett.6b00118. doi:10.1021/acs.estlett.6b00118

Moore, W. S. (2003). Sources and fluxes of submarine groundwater discharge delineated by radium isotopes. *Biogeochemistry*, *66*(1), 75–93. doi:10.1023/B:BIOG.0000006065.77764.a0

Nazaroff, W. W. (1992). Radon transport from soil to air. *Reviews of Geophysics*, *30*(92), 137–160. doi:10.1029/92RG00055

Sajih, M., Bryan, N. D., Livens, F. R., Vaughan, D. J., Descostes, M., Phrommavanh, V., … Morris, K. (2014). Adsorption of radium and barium on goethite and ferrihydrite: A kinetic and surface complexation modelling study. *Geochimica et Cosmochimica Acta*, *146*, 150–163. doi:10.1016/j.gca.2014.10.008

Solomon, D. K., Poreda, R. J., Schiff, S. L., & Cherry, J. A. (1992). Tritium and helium: 3 as groundwater age tracers in the Borden Aquifer. *Water Resources Research*, *28*(3), 741–755. doi:10.1029/91WR02689

Warner, N. R., Christie, C. a., Jackson, R. B., & Vengosh, A. (2013). Impacts of shale gas wastewater disposal on water quality in Western Pennsylvania. *Environmental Science and Technology*, *47*, 11849–11857. doi:10.1021/es402165b