

# **Environmental Management Science Program**

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## **Aquifer Transport of Th, U, Ra, and Rn in Solution and on Colloids**

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### Research Objective

The investigation focuses on understanding the behavior of naturally occurring U, Th, Ra, and Rn isotopes in groundwater along with the supply rates of these isotopes by rock alteration, and utilizing these species as natural analogues for waste radionuclides, thereby providing a basis for predicting contaminant migration behavior in potentially impacted aquifers. The study examines the fundamental controls on natural radionuclide transport in specific aquifers by integrating aquifer sample analyses, focussed laboratory experiments, field observations, and theoretical modeling.

### Research Progress and Implications

The study approach has been to select a reasonably well-characterized aquifer related to a DOE site where groundwaters can be readily collected for analysis of the diverse range of U- and Th-series nuclides and major element chemistry. The field studies to date have focussed on the sandy unconfined aquifer underlying DOE's Brookhaven National Laboratory on Long Island, N.Y., where substantial hydrogeological information is available and where an extensive groundwater monitoring network had been established previously. Groundwater samples were collected from a series of monitoring wells of various depths and nominally along flow paths. Filtration and ultrafiltration techniques were used to concentrate colloids and particles. Samples were analyzed for major element chemistry, short-lived nuclide concentrations by counting techniques and long-lived nuclide concentrations by mass spectrometry.

Significant U concentrations were found at the water table, indicating that substantial amounts of U are supplied to waters percolating through the vadose zone. U concentrations in the aquifer increase and then decrease with distance from the recharge area. Large U isotopic shifts occur in the groundwaters below the water table, while moderate  $^{234}\text{U}$  enrichments are generated within the vadose zone. Colloids  $>10\text{k}$  Daltons account for 40-75% of the U in the aqueous phase and are clearly important carriers of U. The concentrations of dissolved  $^{232}\text{Th}$  are  $\sim 3$  orders of magnitude lower than those of  $^{238}\text{U}$  in the groundwaters, and are close to the predicted thorianite solubility for each sample pH. The amounts of  $^{222}\text{Rn}$  in the water represent 4-20% of the Rn produced in the rock by decay. Where the dissolved  $^{226}\text{Ra}$  concentrations are lower, the dissolved Rn concentration is generally greater, suggesting that higher Rn concentrations in the water are due to increased amounts of  $^{226}\text{Ra}$  on surfaces of the aquifer rock. The activities of the three Ra isotopes are generally comparable to one another in the groundwaters throughout the aquifer and exhibit variations are not systematic but follow those of Ba and appear to be related to groundwater pH. Therefore, sorption processes likely exerts a strong control on dissolved Ra concentrations.

As a guide to interpreting the analytical results, a simple theoretical model has been developed for the transport of U, Th, Ra, and Rn in the vadose zone above the water table and within the aquifer. The model treats the aquifer as three phases: the groundwater; the rock consisting of large grains typical of the aquifer mineralogy and small minor phases in which radioactive elements are concentrated; and a surface layer coating the grains that is available for physico-chemical reactions. The model explicitly considers: transport of radionuclides by advection; physico-chemical exchanges between the groundwater and the reactive surface; and supply of radionuclides by weathering of primary phases and recoil from decay of parent nuclides within aquifer solids. Diffusive transport and lateral mixing are not considered. Self-consistent, one-dimensional equations were developed for the evolution of the radionuclide concentrations in waters percolating through the vadose zone and flowing within the aquifer. Solutions have been obtained for the case where U in the groundwater

does not react with the aquifer solids and Th and Ra are highly surface-reactive, and the evolution of the concentration of these elements along a flow path have been calculated.

A reasonable and consistent set of results have been obtained for general solutions to the model. For groundwater U concentrations and isotopic compositions comparable to those measured in the Long Island aquifer, the model yields weathering rates for the vadose zone that are somewhat higher than those of the aquifer. These rates are consistent with the range of published laboratory results. Rates of release of  $^{234}\text{Th}$  by recoil during decay of parent  $^{238}\text{U}$  that are calculated by the model are consistent with the concentration of U in minor phases within the aquifer solids. These release rates are several orders of magnitude smaller than those obtained for  $^{222}\text{Rn}$ , indicating that Rn release rates cannot be directly applied to all other radionuclides in the decay series, as previously suggested in the literature. Observed decreases in groundwater U concentration with increasing distance are not accounted for by the model; either U is removed by reaction with surfaces or the sampling locations are not along a flowline. Fluctuations in  $^{234}\text{Th}$  and Ra isotope concentrations as well as U isotope compositions cannot be accounted for by model conditions that assume a uniform aquifer, and require variations in aquifer parameters. Major element and radionuclide data indicate that at least one well shows the influence of mixing with water from the underlying aquifer, indicating that the study aquifer is not completely isolated.

## Planned Activities

Further work on the Long Island aquifer in 1998 will include additional sampling to characterize the extent of variability of groundwaters at the water table and between flowlines in the unconfined aquifer, relating the results obtained in this study to available information regarding migrations of other contaminants at the site, and evaluating the possible effects of inflows of water into the aquifer from the underlying deposits. We will increase interactions with the hydrologists at Brookhaven to further integrate the study results with known hydrologic information.

Laboratory experiments are planned for the next year to identify the rates of release of radionuclides from aquifer solids. Initial experiments will examine the controls on the release of  $^{222}\text{Rn}$  from specific radioactive minerals and bulk aquifer solids. Techniques will then be developed to determine the release rates of Th, U, and Ra isotopes. In order to apply the results to aquifer data, measurements will be made on the distribution of radionuclides in specific mineral phases, surface coatings, and leachable sites in aquifer solids.

The work to date has identified the vadose zone as a significant source of radionuclides to the groundwater based on measurements of very shallow groundwaters. Sampling is planned for late 1998 to collect waters from different levels within the vadose zone above one of the aquifer study sites. The concentrations of radionuclides in percolating waters and the distribution of radionuclides in soil solids will be determined. This data will be used to further characterize the mechanisms of radionuclide supply from soil solids, the interactions of radionuclides in percolating waters with solid surfaces, and the rates of radionuclide vertical migration from the surface and into the groundwater.

A sampling program of a second aquifer will be conducted in 1999 to consider radionuclide migration under different aquifer conditions. The well-characterized Edwards aquifer, which supplies water to San Antonio in south-central Texas, is within a limestone that contains both oxic and anoxic conditions and can be readily sampled. Analyses of groundwaters of various ages and chemistries, as well as of core samples that have been obtained from the USGS, are planned. Another aquifer being considered for study is the Great Artesian Basin in Australia, where samples can be collected from the limited recharge areas and along long flow paths in confined layers. Here, it can be determined whether continuous weathering processes continue to add 'conservative' nuclides (e.g.,  $^{234}\text{U}$  and  $^{238}\text{U}$ ) over long flow distances.

Efforts will continue in refining the theoretical framework for understanding radionuclide migration from the surface through the vadose zone and in aquifers under a range of conditions. This will include further developing the present model to include interaction of U with aquifer surfaces, to explicitly incorporate the behavior of colloids, and to include the effects of lateral mixing between flow paths.

## **Other Access To Information**

Tricca, A., Porcelli, D., Wasserburg, G.J., Baskaran, M., and Naidu, J. (1998). Transport of U- and Th-series radionuclides in groundwater. Goldschmidt Conf. Abstr.