Transport of U- and Th-series radionuclides in groundwater

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The purpose of this study is to understand the behaviour of the actinides in groundwater by combining data on the distribution of both long-lived and short-lived nuclides of the U and Th decay series in an aquifer with a model for the nuclide transport along aquifer flow lines. The groundwater concentrations of the short-lived nuclides, such as ^{222}Rn, ^{224}Ra and ^{234}Th, provide information only on local aquifer conditions, while the concentrations of the long-lived nuclides reflect geochemical processes along extended flow paths. In an important study, Krishnaswami *et al.* (1982) calculated sorption rate constants for many of the decay series nuclides in an aquifer using a batch model. However, no study yet has combined the data provided by both long and short-lived radionuclides to study the transport mechanisms along a flow line. Furthermore, although colloidal phases have been found to be important carriers of U and Th in numerous natural aqueous systems, very few investigations have been conducted on their importance in the transport of naturally-occurring actinides in groundwater.

The aquifer investigated here is the sandy unconfined Upper Glacial Pleistocene aquifer situated in Long Island, NY. Extensive information regarding the geology and the hydrology of the aquifer is available and numerous high quality and well-documented wells are available for sample collection. This aquifer is underlain by a discontinuous layer of impermeable clay, below which is a sandy confined aquifer, the Magothy, where reducing conditions prevail. Radionuclide data from several wells in this aquifer have been reported by Copenhaver *et al.* (1993). Samples from the Upper Glacial aquifer have been taken along two flow lines at three different depths and filtered through 0.45 μm filter cartridges. In addition, cross-flow ultrafiltration has been used to separate colloids >10 kD from ultrafiltered water that represents the dissolved load. This technique, described in previous papers, has proven to be successful in studying the association of uranium and other elements with colloids (e.g. Porcelli *et al.*, 1997). The concentrations of the long-lived radionuclides ^{238}U, ^{234}U and ^{232}Th have been measured by thermal ionization mass spectrometry and the short-lived radiogenic daughters ^{222}Rn, ^{226}Ra, ^{228}Ra, ^{224}Ra, ^{234}Th by counting methods. In addition, the water samples have been analysed for pH and conductivity in the field, and for concentrations of major cations, anions and trace elements.

Water samples from the Upper Glacial aquifer have pH values of 5.4 to 6.5 and TDS (Total Dissolved Solid) of 20 to 100 mg/l. The high Mn concentration in a deep sample of the shallow aquifer likely indicates a difference in redox conditions. The Magothy aquifer has TDS of ~ 50 mg/l, comparable to that of the unconfined aquifer, but much higher Fe and Mn concentrations.

The ^{222}Rn activities generally full within a restricted range throughout the Upper Glacial aquifer of 65 to 170 dpm/kg, with two peak values of 336 and 522 dpm/kg. The amount of Rn in the water represents ~4 % of the Rn produced in the rock by decay. Assuming that the aquifer rock consists of solid spherical grains with uniform distribution of Ra, this amount of Rn can only be supplied by grains of ~ 0.1 μm in size and therefore cannot be produced by the aquifer which average grain size is ~1 mm. This has been observed previously (e.g. Copenhaver *et al.*, 1993). High Rn concentrations have been observed and lead to the requirement that Rn is circulating through nanopores or that the source of Rn is on the surface. We observe that the dissolved Rn concentration is generally greater where the dissolved ^{226}Ra concentration is lower, suggesting that higher Rn concentrations in the water are due to increased amounts of ^{226}Ra on aquifer surfaces due to deposition of dissolved ^{226}Ra. Therefore we infer that Rn concentrations here are controlled by the distribution of Ra on surfaces rather than by enhanced release from throughout the aquifer grains by nanopores (Rama and Moore, 1984). The supply of other daughter nuclides into the ground water requires similar considerations of the redistribution of parent nuclides and cannot be directly derived from the supply of ^{222}Rn (compare with Krishnaswami *et al.*, 1982).

The 0.45 μm-filtered Upper Glacial water samples have U concentrations of between 2.8 and 16.3 ng/kg and δ^{234}U of 46 to 1394‰. These concentrations first increase and then decrease along each flow line, requiring both U addition and removal, thus demonstrating the nonconservative behaviour of U in the groundwater. In the sample with the highest U concentration, it has been found that colloids carry ~ 75% of the U in the <0.45 μm fraction. The Magothy water has the highest U concentration, of 25.3 ng/kg, and is characterized by a δ^{234}U value of 197‰. Here again the colloids play a major role, with ~50% of the U and ~30% of the Fe associated with the colloidal fraction. Thus, the U increase in the Upper Glacial aquifer might be due to an input of U-bearing colloids and the subsequent decrease along the flow line to their removal. The ultrafiltered fractions have U isotopic compositions indistinguishable from those of the corresponding 0.45 μm filtered fractions, so that rapid isotopic exchange must occur between the colloidal and dissolved phase. Since colloids appear to be a major carrier of U in groundwater, information on their origin, migration, and removal is a key to an understanding of the transport of U-Th series nuclides in ground water.

The concentrations of ^{232}Th vary between 14 and 165 pg/kg and are 3 orders of magnitude lower than that of ^{238}U in the shallower ground water. These concentrations are close to the predicted thorianite solubility for each sample pH. In contrast, the Magothy water exhibits much higher ^{232}Th concentration of 8.8 ng/kg indicating enhanced transport of Th under the reducing conditions of this aquifer. The measured ^{234}Th activities do not vary significantly in the Upper Glacial aquifer, with concentrations ~ 20×10^{-3} dpm/kg in the dissolved phase (with one higher value of 74×10^{-3} dpm/kg). The Magothy water shows a comparable ^{234}Th activity of 33×10^{-3} dpm/kg, indicating a similar ^{234}Th recoil rate into solution. This is compatible with a constant recoil supply of ^{234}Th into the groundwater from decay of ^{238}U in aquifer solids. The dissolved ^{234}Th concentrations are insufficient to generate the excess ^{234}U in the Upper Glacial ground water. We suggest that the excess ^{234}U may be largely produced by ^{234}Th adsorbed onto aquifer surfaces.

The activities of the three radium isotopes, ^{228}Ra, ^{224}Ra and ^{226}Ra are comparable to one another and vary over a range of 26 to 193×10^{-3} dpm/kg. All three isotopes exhibit the same variations along the flow lines despite their very different half-lives. These variations are not systematic but follow those of Ba. They appear to be controlled by sorption processes, based upon their relationship with pH in the water.

A model has been developed for the transport of the U and Th decay series nuclides along a one-dimensional flow path within an aquifer with defined porosity, primary aquifer phase nuclide concentrations, and a reactive surface area per unit volume. The model explicitly considers transport of radionuclides by advection, weathering of the primary phases, radioactive decay, physico-chemical exchanges between the ground water and the aquifer surfaces expressed as kinetic reactions taking place at the reactive surface of the solid, and recoil of nuclides into the water from decay of parent nuclides both within the primary aquifer phase and adsorbed onto aquifer surfaces. By solving the full transport equations that include these processes, the concentration of each radionuclide of the U-Th decay series in solution and adsorbed on aquifer surfaces along a flow line could be expressed as a function of the porosity, the average linear groundwater flow velocity, the weathering rate, the radionuclide decay constants, the recoil fraction and the rate constants of the sorption reactions. The evolutionary trends of the radionuclide concentrations along a flow line for different parameter values have been investigated. Comparison of the model results with the measurements of the Long Island aquifer are used to estimate parameter values that may apply to the aquifer and to suggest the processes responsible for deviations from simple model evolutionary paths.

We thank Doug Paquette, Rich Lagattolla and the environmental division personnel from Brookhaven National Laboratory who provided valuable help during our sampling effort. This work was funded by DOE grant #DE-FG07-96ER14700. This is contribution # 8517(997)

References

Krishnaswami, S. Graustein, W.S. and Turekian, K. (1982) *Water Resource Research*, **18**, 1663–75.

Porcelli, D. Andersson, P.S., Wasserburg, G.J., Ingri, J. and Baskaran, M. (1997) *Geochim. Cosmochim. Acta*, **61**, 4095–113.

Copenhaver, S.A., Krishnaswami, S., Turekian, K., Epler, N. and Cochran, J.K. (1993) *Geochim. Cosmochim. Acta*, **57**, 597–603.

Rama and Moore, W.S. (1984) *Geochim. Cosmochim. Acta*, **48**, 395–9.