Characterization of Contaminant Transport Using Naturally-Occurring U-Series Disequilibria: In-Situ Radionuclide Transport and Preferential Groundwater flow at INEEL (Idaho)

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Abstract — Uranium- and thorium-decay series disequilibria in groundwater occur as a result of water-rock interactions, and they provide site-specific, natural analog information for assessment of in-situ, long-term migration of radionuclides in the far field of a nuclear waste disposal site. In this study, a mass balance model was used to relate the decay-series radionuclide distributions among solution, sorbed and solid phases in an aquifer system to processes of water transport, sorption-desorption, dissolution-precipitation, radioactive ingrowth-decay, and alpha- recoil. Isotopes of U (U-238, 234), Th (Th-232, 230, 228, 234), Ra (Ra-226, 228, 224), and Rn (Rn-222) were measured in 23 groundwater samples collected from a basaltic aquifer at the Idaho National Engineering and Environmental Laboratory (INEEL), Idaho. The results show that groundwater activities of Th and Ra isotopes are 2-4 orders lower than those of their U progenitors which average 1.35±0.40 dpm U-238/L, with U-234/U-238 ratios of ~1 6-3.0. Rn-222 activities range from 20 to 500 dpm/L. Modeling of the observed disequilibria places the following constraints on the time scale of radionuclide migration and water-rock interaction at INEEL: (1) Time for sorption is minutes for Ra and Th; time for desorption is days for Ra and years for Th; and time for precipitation is days for Th, years for Ra, and centuries for U. (2) Retardation factors due to sorption average >10^6 for Th-232, ~10^4 for Ra-226, and ~10^3 for U-238. (3) Dissolution rates of rocks are ~70 to 800 mg/L/y. (4) Ages of groundwater range from <10 to 100 years. Contours of groundwater age, as well as spatial patterns of radionuclide disequilibria, delineate two north-south preferential flow pathways and two stagnated locales. Relatively high rates of dissolution and precipitation and alpha-recoil of Rn-222 occur near the groundwater recharging sites as well as in the major flow pathways. Decay of the sorbed parent radionuclides (e.g., Ra-226 and Ra-228) on micro-fracture surfaces constitutes an important source of their daughter (Rn-222 and Th-228) activities in groundwater.

A. Introduction

The project is a collaborated research between the University of Southern California (USC) and the Los Alamos National Laboratory (LANL). Here we present mainly the works performed by the USC group.

The Idaho National Engineering and Environmental Laboratory (INEEL) is a Department of Energy facility that encompasses approximately 2300 km^2 in the west-central part of the Eastern Snake River Plain. Since the early 1950s, low-level radioactive and non-radioactive waste was disposed of via injection wells that penetrate to the aquifer. Contaminant plumes extend downgradient from these injection wells and some contaminants can be tracked to near the southern boundary of the site. In addition, there are several surface and shallowly buried waste storage sites that have released contaminants to the environment. Concerns about existing and potential additional contamination of the aquifer have prompted numerous studies to better understand groundwater flow and contaminant migration in the aquifer. This research is directed toward an assessment of rates of the water-rock-radionuclide interactions, the preferential groundwater flow paths, and the transport of radionuclides in fracture-rock systems using a natural analog approach. It falls under one of the five focused topical areas of the ER/EM Collaborative Research Program (Topic 1 of the ER/EM Collaborative Research Solicitation: September 1995).

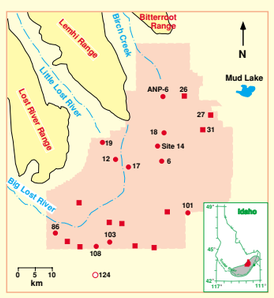

Fig. 1 Map showing the sampling locations. Sampling times (see Table 1) are indicated by different symbols: open circle (Apr. 10, 1997); solid circles (Sept. 12 to 17, 1997); and solid squares (Aug. 26 to Sept. 10, 1998). The boundary of the INEEL site and three ephemeral rivers in the area are marked by dashed and dashed-dotted lines, respectively. Hatched areas represent mountain ranges. The inset shows the locations of INEEL (blackened area) and the Snake River Plain Aquifer (shaded area) in Idaho, USA.

B. Objectives

The goal of the research is to study the migration of nuclear waste contaminants in subsurface fractured systems using naturally occurring uranium- and thorium-series radionuclides as tracers under in-situ physico-chemical and hydrogeologic conditions. We develop a model of contaminant migration in the Snake River Plain Aquifer beneath the INEEL by evaluating the retardation processes involved in the rock/water interaction. The major tasks are to determine: (1) the distribution of U, Th, Pa, Ra, Rn, Po and Po isotopes in groundwater as well as in rock minerals and sorbed phases, (2) through modeling the extent of disequilibria the in-situ retardation factors of radionuclides and rock/water interaction time scales, and (3) the water residence time in the aquifer and the preferential flow paths. The study provides an improved characterization of preferential flow and contaminant transport in fractured rocks — information that pertains to risk and performance assessment and remediation action at INEEL and other contaminated DOE sites.

C. U-series Disequilibrium Model

Model assumes:

(1) first-order kinetics govern sorption-desorption and dissolution-precipitation of radionuclides, i.e., a linear sorption isotherm for the range of concentrations of the nuclides in groundwater

(2) alpha- recoil input from the sorbed and dissolved pools to the solid pool is negligible.

(3) decay of radionuclides on rock surface releases all daughter nuclides into the dissolved pool.

Steady-state mass balance equation:

$$Q + P_d + P_r + \lambda R_f C' = k_p C + \lambda R_f C \qquad (1)$$

Where C = Concentration of a Radionuclide in groundwater
Q = supply or removal rate by water transport
P_d = supply rate by dissolution
P_r = supply rate by alpha recoil
λ = decay constant
R_f = retardation factor
k_p = precipitation rate constant
(Prime notation refers to the parent nuclide)

$$R_f = 1 + k_1/(k_2+\lambda) \qquad (2)$$

where R_f = in-situ retardation factor , with k_1 and k_2 being sorption and desorption rate constants, respectively.

$$Q = (C_i - C)/\tau_w \qquad (3)$$

where τ_w = groundwater transient time
C_i = radionuclide concentration in source waters

Model Input

Measured activities of isotopes in groundwater
U (238U, 234U)
Th (232Th, 230Th, 228Th , 234Th)
Ra (226Ra, 228Ra, 224Ra)
Rn (222Ra)

Known values for the INEEL site (Knobel et al, 1995):
232Th activity in rocks = 0.31±0.02 dpm/g
238U/232Th ratio in rocks = 0.90±0.06

Model Output

- Fluid transient times and preferential flow paths
- Retardation factors of Ra, Th, and U isotopes
- Adsorption and desorption rates of Ra and Th
  - Rock dissolution rates
  - Precipitation rates of Th, Ra and U

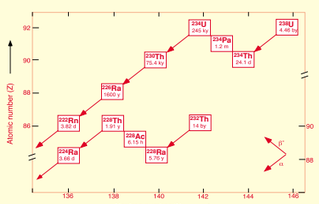

Fig. 2 Parts of the U-238 and Th-232 decay chains showing the isotopes under study.

D. Results

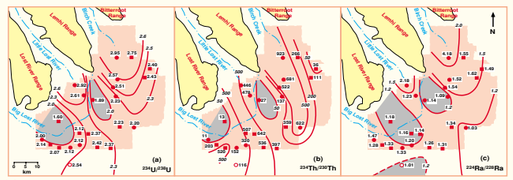

Fig 3

Fig. 3 Distributions of (a) 234U/238U, (b) 228Th/232Th, and (c) 224Ra/228Ra activity ratios in INEEL groundwater, all showing southward decreases along two preferential flow paths with minimum values occurring just south of Lost River and Lemhi Ranges. The general similarities among the three plots reflect a linkage between aging of groundwater, degree of rock weathering, and intensity of alpha-recoil radionuclide flux in the aquifer. The shaded areas encircled (or semi-encircled) by the contour lines denote "low" values inside.

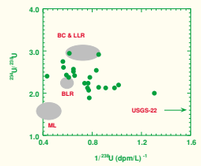

Fig. 4 Plot of 234U/238U vs. 1/238U in groundwater. The hatched areas represent the U isotopic composition of different source waters from the Birch Creek and Little Lost River drainages (BC & LLR), Big Lost River (BLR), and the Mud Lake region (ML). Arrow indicates that values of 234U/238U and 1/238U for well USGS-22 (1.6 and 3.1) fall outside the range of the abscissa. The plot shows that the observed isotopic compositions cannot be explained by mixing of the water masses.

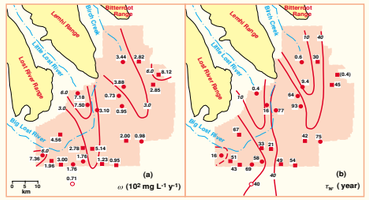

Fig. 9 Variations of (a) rock dissolution rate (ω) and (b) groundwater residence time (τw). In (b), the contours delineate two preferential (fast) groundwater flows migrating southward from the recharge areas where the Birch Creek and Little Lost River submerge (The parenthesized number at USGS 27 is anomalous; see Fig. 8 for explanation.) The flows are confined to narrow channels upon reaching the south boundary of INEEL. In (a), rock dissolution rate decreases along the major flow paths showing a spatial pattern similar to that shown in (b). High dissolution rates occur at the recharge regions and are usually accompanied by high precipitation rates (see Fig. 8), suggesting enhanced weathering of rocks in contact with young groundwater.

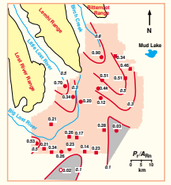

Fig. 5 Distribution of Pr/ARn222, showing that only a small fraction of 222Rn in the groundwater at INEEL is contributed by alpha-recoil. This contribution diminishes southward along the preferential flow paths, with lowest Pr/ARn222 values occurring in the south and southeast. The shaded areas encircled (or semi-encircled) by the contour lines denote "low" values inside.

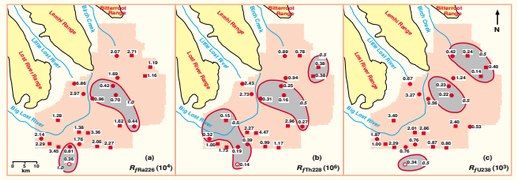

Fig. 7 Distributions of in-situ retardation factor (R_f) of (a) 226Ra, (b) 228Th, and (c) 238U. The shaded areas encircled (or semi-encircled) by the contour lines denote "low" values inside. Retardation factors average about 10^6 for 228Th, 10^4 for 226Ra, and 10^3 for 238U. It is estimated from these results that the desorption rate constant of Th is about 2 orders smaller than that of Ra, while their sorption rate constants are similar.

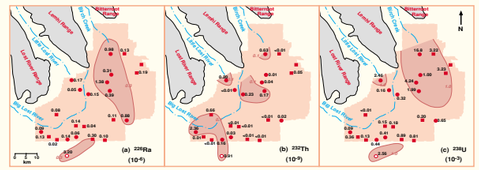

Fig. 10 Transport rates of radionuclides by groundwater relative to those by precipitation and/or radioactive decay: (a) 226Ra, (b) 228Th, and (c) 238U. The shaded areas encircled (or semi-encircled) by the contour lines denote "high" values inside.

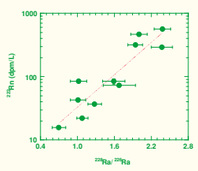

Fig. 6 Relationship between 222Rn and 228Ra/226Ra in groundwater. The straight line is the least-squares fit to the data by the relationship:
222Rn (dpm/L) = 4.64 exp[1.96x(228Ra/226Ra)]

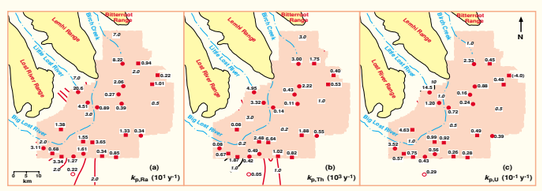

Fig. 8 Variations in precipitation rate constants (k_p) of (a) radium, (b) thorium, and (c) uranium. In (c), the parenthesized number at USGS 27 is anomalous probably due to enhanced U dissolution associated with agriculture activities. Consistent regional variations exist, i.e., large k_p values occur chiefly near the recharge areas and decrease southward along the preferential flow paths. Older groundwaters typically have smaller k_p values. The shaded areas encircled (or semi-encircled) by the contour lines denote "low" values inside.

E. Conclusions

This study, by providing for the first time a comprehensive and quantitative assessment of the in-situ migration rates of radionuclides in the groundwater of a DOE site, shows that the naturally-occurring decay-series isotopes in groundwater are uniquely suited for study of site-specific, long-term transport of nuclear wastes in the groundwater. The study reveals the importance of dissolution and precipitation in controlling the transport of radionuclides in groundwater which are difficult to ascertain through lab experiments. Recognizing the role of a sorbed pool of radionuclides in aquifer rocks by this study cautions us in the use of batch experiments to determine distribution coefficients of radionuclides, as many of the surface sorption sites on rocks are formed in nature over geological time scales.

Information Access

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- Luo S., Ku T. L., Roback R., Murrell M. T., and McLing T. (2000)Geochim. Cosmochim. Acta, 64, 867-881.
- Luo S., Ku T. L., Roback R., Murrell M. T., and McLing T. (in press) in: Scientific Basis for Nuclear Waste Management XXIII, proceedings vol. 608 of the Materials Research Society Symposium Proceedings Series.
- E-prints: http://emsp.em.doe.gov