DECAY-SERIES DISEQUILIBRIUM STUDY OF IN-SITU, LONG-TERM RADIONUCLIDE TRANSPORT IN WATER-ROCK SYSTEMS

SHANGDE. LUO*, TEH-LUNG KU*, ROBERT ROBACK‡, MICHEAL MURRELL‡, TRAVIS L. MCLING¶

* Dept. of Earth Sciences, Univ. of Southern California, Los Angeles, CA 90089-0740, sluo@usc.edu

‡ MSJ 514, Los Alamos National Laboratory, Los Alamos, NM 87545

¶ Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID 83415-2107

ABSTRACT

Uranium and thorium-series disequilibrium in nature permits the determination of many *in-situ* physico-chemical, geologic and hydrologic variables that control the long-term migration of radionuclides in geologic systems. It also provides site-specific, natural analog information valuable to the assessment of geologic disposal of nuclear wastes. In this study, a model that relates the decay-series radioisotope distributions among solution, sorbed and solid phases in water-rock systems to processes of water transport, sorption-desorption, dissolution-precipitation, radioactive ingrowth-decay, and α recoil is discussed and applied to a basaltic aquifer at the Idaho National Engineering and Environmental Laboratory (INEEL), Idaho.

INTRODUCTION

Performance assessment models for nuclear waste disposal generally invoke laboratory-derived distribution coefficients (K_d) for individual radioelements to simulate radionuclide migration. Questions can be raised as to the extent to which laboratory data reflect the behavior of natural geochemical systems because of K_d dependence on properties such as groundwater chemistry, aquifer mineralogy, colloidal presence, and microbial activities in the system. Natural analog studies in geological environments provide an alternative approach to model testing and validation. Application of this approach to undisturbed systems allows an in-situ assessment of long-term migration behaviors of radionuclides. Naturally occurring uranium and thorium series radionuclides are well suited for such studies because several isotopes of the same element continuously enter groundwaters and because the supply rate of many of these radionuclides can be estimated with adequate accuracy [1]. In what follows we will show that a variety of chemical, geologic and hydrologic processes that control radionuclide transport can be understood through modeling the decay-series disequilibria observed in a natural system.

MODELING THE URANIUM- AND THORIUM-SERIES DISEQUILIBRIUM

In commenting on the use of decay-series disequilibria as natural analogs for nuclide movements in groundwater system, McKinley and Alexander [2] have cited the failure of previous attempts to distinguish (1) the process of sorption from precipitation, and (2) sorbed species from those present inside mineral grains or precipitates that are impermeable to water. To address their concerns, Ku et al. [3] proposed a model that relates the steady-state distributions of decay-series nuclides in dissolved, sorbed, and solid pools of a geologic system to in-situ processes of water transport, sorption-desorption, dissolution-precipitation, radioactive ingrowth-decay, and α recoil. The model has the following mathematical expression:

$$Q + P_d + P_r + R_f^p A^p = k_p C + R_f A \qquad (1)$$

where A ($=\lambda C$; λ is the decay constant and C the concentration) is the nuclide activity in groundwater (dpm L^{-1}), with superscript p referring to its radioactive parent; k_p is the precipitation rate constant (y^{-1}); Q, P_d, and P_r are the rates (atoms L^{-1} y^{-1}) of supply by water flow, dissolution, and α recoil, respectively; and R_f is the retardation factor, expressed as:

$$R_f = 1 + K = 1 + \frac{k_1}{k_2+\lambda} \qquad (2)$$

where K is a dimensionless distribution coefficient between the sorbed and dissolved pools for the radionuclide that has k_1 and k_2 as its sorption and desorption rate constants (y^{-1}), respectively. The model assumes that (1) first-order kinetics govern the processes of sorption-desorption and dissolution-precipitation of radionuclides (It can be shown that dissolution is reduced to zeroth order for a constant radionuclide concentration in the solid pool) and (2) α-recoil input from the sorbed and dissolved pools to the solid pool is negligible. Implicit in assumption (1) is a linear sorption isotherm for the range of concentrations of the nuclides of interests. For R_f to be independent of nuclide concentrations, it is also assumed that decay of radionuclides on the rock surface (the sorbed pool) releases all daughter nuclides into the dissolved pool. The validity of these assumptions has been assessed by Ku et al. [3] and Murphy [4]. In this paper, the model is applied to characterize the nuclide transport in groundwaters at the Idaho National Engineering and Environmental Laboratory (INEEL), Idaho (Fig. 1).

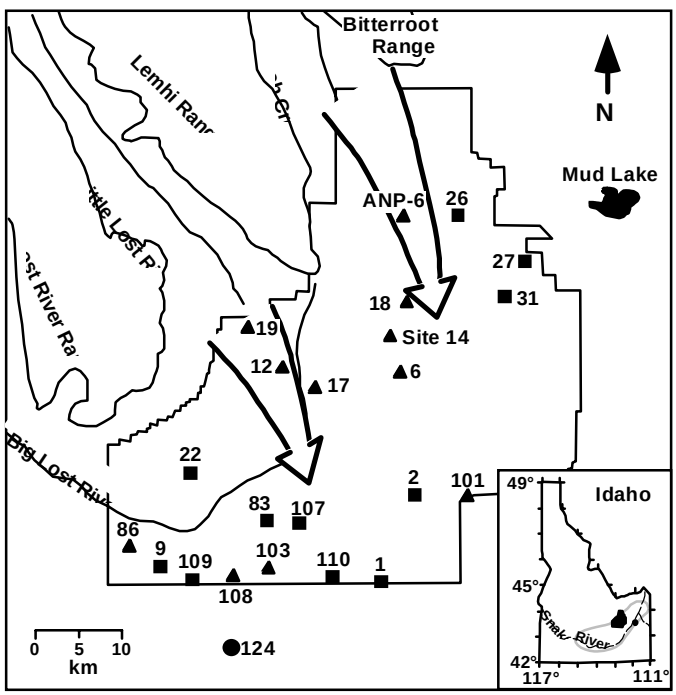

Fig. 1. Map showing the sampling locations. Groundwaters were sampled on Apr. 10, 1997 (circles), Sept. 12–17, 1997 (triangles) of 1997, and Aug. 26–Sept. 10, 1998 (squares) for measurements of U, Th, Ra and Rn isotopes [5]. The two large arrows indicate the major groundwater pathways as delineated by the modeling results. The inset shows the locations of INEEL (blackened area) and the Snake River Plain Aquifer (shaded area) in Idaho, USA. The groundwater is unconfined, contains <325 mg/L of dissolved solutes, and with typical pH of ~8.0 and Eh of ~227 mV, is mostly of the Ca-Na-bicarbonate type, relatively high in silica, and saturated in dissolved oxygen [5].

Equation (1) can be simplified by setting $Q = 0$ for isotopes of Th (^{232}Th, ^{230}Th, ^{228}Th, and ^{234}Th) and Ra (^{226}Ra, ^{228}Ra, and ^{224}Ra) because of their affinity to aquifer solids in geologic environments. Thus,

$$P_d + P_r + R_f^p A^p = k_p C + R_f A \qquad (3)$$

The rate of dissolution of a nuclide from rocks (P_d) is the product of rock dissolution rate (ω, g L^{-1} y^{-1}) and the nuclide concentration (C^r, atoms g^{-1}) in rocks. The number of atoms of a decay-series radionuclide in solutions or in rocks generally decreases with increasing the nuclide's decay constant. Therefore, for short-lived radionuclides such as ^{228}Th, ^{234}Th, ^{228}Ra, ^{224}Ra and ^{222}Rn, dissolution and precipitation can be neglected, giving:

Table I. Measured decay-series isotope activities (dpm/m^3) and activity ratios in groundwater at INEEL, Idaho*

Well No.	^{238}U ($\infty 10^3$)	^{232}Th	^{226}Ra	^{222}Rn ($\infty 10^3$)	^{234}U/^{238}U	^{234}Th/^{238}U	^{230}Th/^{232}Th	^{228}Th/^{232}Th	^{228}Th/^{228}Ra	^{228}Ra/^{226}Ra	^{224}Ra/^{228}Ra
USGS-124	1.200	0.492	47.2	(170)	2.54	0.056	1.18	4.6	0.068	1.84	1.01
USGS-86	0.765	2.761	18.8	(860)	2.00	0.036	0.95	1.2	0.068	2.66	1.47
USGS-101	0.987	0.055	10.9	(50)	2.20	0.043	1.23	3.9	0.016	1.21	1.03
USGS-103	1.099	0.110	5.1	(117)	2.12	0.038	1.18	3.4	0.045	1.65	1.20
USGS-108	1.311	0.129	4.3	(47)	2.12	0.019	1.25	1.7	0.044	1.19	1.33
USGS-19	1.173	0.045	1.5	(346)	2.92	0.017	1.00	2.1	0.028	2.20	2.18
USGS-12	1.763	0.070	14.0	(632)	2.61	0.028	1.46	5.5	0.011	2.51	1.23
ANP-6	1.630	0.035	7.4	(1455)	2.95	0.024	1.18	14.3	0.023	2.93	4.18
USGS-17	1.288	0.686	17.4	(209)	1.89	0.015	1.01	1.5	0.031	1.94	1.14
Site 14	1.545	0.053	14.9	(112)	2.51	0.023	1.27	7.7	0.017	1.62	1.54
USGS-18	1.540	0.054	10.4	(361)	2.57	0.031	1.27	7.6	0.018	2.22	1.52
USGS-6	1.306	0.266	14.5	(114)	2.23	0.029	1.06	3.8	0.042	1.63	1.09
USGS-110	1.516	0.037	14.3	16	2.42	0.021	1.59	5.6	0.021	0.70	1.26
USGS-2	1.356	0.033	15.3	37	2.23	0.017	1.89	3.3	0.006	1.28	1.34
USGS-107	1.640	0.024	8.5	84	2.37	0.014	1.50	4.2	0.008	1.59	1.14
USGS-83	1.019	0.035	18.4	565	2.12	0.023	1.32	7.7	0.006	2.38	1.16
USGS-22	0.323	1.754	19.3	293	1.60	0.071	0.99	2.2	0.084	2.37	1.18
USGS-1	1.279	0.036	11.6	22	2.37	0.017	1.53	6.7	0.019	1.08	1.31
USGS-9	1.175	0.090	11.9	85	2.14	0.019	1.23	3.1	0.023	1.02	1.28
USGS-109	1.293	0.051	6.6	73	2.07	0.029	1.45	4.4	0.020	1.68	1.33
USGS-27	2.310	0.628	15.6	465	2.40	0.010	0.98	1.5	0.031	1.94	1.49
USGS-31	1.695	0.167	13.9	314	2.43	0.010	0.96	5.2	0.031	2.00	1.62
USGS-26	1.780	0.050	8.4	42	2.75	0.007	1.00	5.9	0.035	1.01	1.55

* Except for ^{238}U which was measured by thermal ionization mass spectrometry, all isotopes were measured by decay counting techniques [5]. The analytical errors (1-σ) derived from counting statistics were <0.5 % for ^{238}U, <5 % for ^{234}U, ^{234}Th, ^{228}Th, ^{226}Ra, ^{228}Ra, ^{224}Ra and ^{222}Rn, and about 3-10 % for ^{230}Th and ^{232}Th. Data in parentheses are interpolated values from the observed relationship between ^{228}Ra/^{226}Ra and ^{222}Rn [5].

$$P_r + R_f^p A^p = R_f A \tag{4}$$

Because $P_r \bullet 0$ for β-decay products, applying eqn. (4) to ^{228}Th relates the retardation factors of ^{228}Th and ^{228}Ra to their activity ratio (A_{Ra228}/A_{Th228}) in groundwater as:

$$\frac{R_{f,Th228}}{R_{f,Ra228}} = \frac{A_{Ra228}}{A_{Th228}} \tag{5}$$

For uranium isotopes ^{238}U and ^{234}U, eqn. (1) is used to estimate Q (atoms L^{-1} y^{-1}) and the groundwater transit time (τ_w, y) is related to Q by the relationship:

$$Q = \frac{\left(C^i - C\right)}{\tau_w} \tag{6}$$

where C^i is the radionuclide concentration in recharging waters (atoms L^{-1}). Positive values of Q denote net gain due to fluid transport.

Equations (1) – (6) form the basis of our assessment of the effects of sorption-desorption, dissolution-precipitation, and advection-diffusion in the radionuclide transport in groundwater. The α-recoil input (P_r) can be determined from the groundwater ^{222}Rn activities [1]. The relationships depicted by the above equations allow us to determine retardation factors (R_f) of U, Th and Ra from measurements of short-lived Ra and Th isotopes, as well as the rock dissolution rate (ω), the precipitation rate constants (k_p) of U, Th and Ra, and the groundwater transit time (τ_w) from measurements of long-lived U, Th, and Ra isotopes.

RESULTS AND DISCUSSION

Table I shows the measurement results of isotopes of U (^{238}U, ^{234}U), Th (^{232}Th, ^{230}Th, ^{228}Th, ^{234}Th), Ra (^{226}Ra, ^{228}Ra, ^{224}Ra) , and Rn (^{222}Rn) in groundwaters collected from a basaltic aquifer at INEEL, Idaho (Fig. 1). A very large range of activities exists: from 10^4 -10^6 dpm m^{-3} for ^{222}Rn, to 10^3 dpm m^{-3} for ^{238}U and ^{234}U, to 10-10^2 dpm m^{-3} for ^{226}Ra, ^{228}Ra, ^{224}Ra, and ^{234}Th, and to less than 1 dpm m^{-3} for ^{232}Th, ^{230}Th, and ^{228}Th. Radioactive disequilibria among the radionuclides occurred as a result of water-rock interaction. Applying the observed disequilibria to the model presented above, we have made estimates on rates of α recoil, sorption-desorption, and dissolution-precipitation; in-situ retardation factors of isotopes of U, Th and Ra; and water transit time in the aquifer. The major results are summarized in Table II.

Alpha-Recoil Input

The model-derived α-recoil rates show great regional variations. Given an α-recoil range of ~0.05 µm, rock density of ~2.8 g cm^{-3} and ^{238}U activity of 0.3 dpm g^{-1} in basalt at INEEL[5, 6], these rates can be translated to an effective surface area (S) of the aquifer rocks in the range (2-1300)$\infty 10^6$ cm^2 L^{-1}, equivalent to a fracture width of ~0.02-10 µm for a planar structure or a pore diameter of ~0.04-20 µm for a tubular configuration. Relatively large fractures occur in the southern part of INEEL.

The α-recoil rates (Table II) are significantly lower than the ^{222}Rn activities in groundwater (Table I), suggesting that the in-situ production from decay of ^{226}Ra in the dissolved and sorbed pools must contribute an important source of ^{222}Rn to groundwater. This is particularly true for those waters from the southern part of INEEL, in which the ^{222}Rn

activities are low and the $P_{r,Rn222}/A_{Rn222}$ ratios are mostly close to ~0.1. The U and Th concentrations in rocks vary only slightly throughout the study area and are typical of those for basalts [6]. It is therefore the fracture size and density, not the chemical compositions, of the aquifer rocks that exert a main control on the supply rate of ^{222}Rn by α-recoil.

Retardation Factors of Ra, Th and U

Ra isotopes: In spite of their vastly different half lives, the Ra isotopes ^{226}Ra, ^{228}Ra and ^{224}Ra should have similar R_f values because rapid desorption rate of radium is inferred from the following model equation [5]:

$$P_{r,\,Ra224} + R_{f,Ra228}\,A_{Ra228} = R_{f,Ra224}\,A_{Ra224} \qquad (7)$$

For most of the samples, A_{Ra224} is only slightly higher than A_{Ra228} (Table I). Equation (2) requires $R_{f,Ra228} \bullet R_{f,Ra224}$. To meet these requirements, eqn. (7) shows that the recoil input of ^{224}Ra from the basaltic aquifer rocks must be small and $R_{f,Ra228} \bullet R_{f,Ra224}$, i.e., the desorption rate constant (k_2) of Ra must be much greater than the decay constant of ^{224}Ra (= 0.19 day^{-1}). Thus we have: $R_{f,Ra224} = R_{f,Ra228} = R_{f,Ra226} = R_{f,Ra}$. It is also inferred that the activity of ^{224}Ra in any groundwater should not be smaller than that of ^{228}Ra . However, because of the short half life of ^{224}Ra, aging of water in well bores (e.g., if wells are not completely purged before sampling) or in large fractures may cause the ^{224}Ra /^{228}Ra ratio to become <1.

Table II. Model-derived α-recoil rate (P_r, atoms L^{-1}min^{-1}) of ^{222}Rn, retardation factors (R_f) and precipitation rate constants (k_p, y^{-1}) of Ra, Th, and U, rock dissolution rate (ω, mg L^{-1}y^{-1}), and water transit time (τ_w, y)*

Well No.	$P_r \infty 10^{-2}$	$R_f \infty 10^{-4}$ (Ra)	$R_f \infty 10^{-6}$ (^{232}Th)	$R_f \infty 10^{-6}$ (^{228}Th)	$R_f \infty 10^{-6}$ (^{224}Th)	$R_f \infty 10^{-3}$ (U)	$k_p \infty 10^{-3}$ (Th)	$k_p \infty 10^{-1}$ (Ra)	$k_p \infty 10$ (U)	ω	τ_w
USGS-124	0.02	0.36	0.62	0.14	0.006	0.34	0.04	0.22	0.29	71	39.8
USGS-86	4.56	2.14	**	0.32	0.051	1.87	0.08	3.11	3.52	736	16.2
USGS-101	0.02	0.44	1.03	0.27	0.013	0.53	0.55	0.34	0.39	98	75.3
USGS-103	0.27	1.76	1.07	0.39	0.021	0.76	0.49	1.61	0.56	176	57.5
USGS-108	0.13	0.81	0.21	0.19	0.041	0.76	0.42	1.27	0.43	176	69.4
USGS-19	2.43	6.86	**	2.43	0.051	0.67	4.95	20.57	14.48	718	0.4
USGS-12	2.16	2.97	11.50	2.73	0.123	3.27	3.32	4.51	1.20	750	15.6
ANP-6	13.02	2.07	**	0.89	0.051	0.42	3.00	8.22	2.33	344	0.6
USGS-17	0.41	0.96	0.41	0.31	0.040	0.56	0.14	0.88	0.72	310	76.9
Site 14	0.50	0.42	0.87	0.25	0.012	0.23	0.42	0.27	0.16	73	64.4
USGS-18	1.85	1.69	3.41	0.94	0.044	1.24	2.22	2.06	0.88	388	9.4
USGS-6	0.13	0.70	0.57	0.16	0.008	0.22	0.11	0.40	0.24	95	92.9
USGS-110	0.02	2.06	5.47	0.99	0.041	0.87	1.02	0.33	0.26	123	48.8
USGS-2	0.10	1.62	9.23	2.92	0.146	2.40	1.88	1.33	0.49	200	41.6
USGS-107	0.14	3.36	18.27	4.47	0.202	2.84	6.64	3.65	0.92	514	21.1
USGS-83	1.47	1.38	12.78	2.27	0.094	2.01	2.48	1.55	0.99	278	33.3
USGS-22	0.83	1.28	**	0.15	0.051	3.40	0.08	1.38	4.63	456	66.8
USGS-1	0.05	2.27	7.73	1.17	0.047	0.80	0.82	0.85	0.28	95	53.8

USGS-9	0.18	2.29	2.87	1.00	0.052	0.97	0.67	0.68	0.57	196	50.7
USGS-109	0.24	3.45	7.03	1.73	0.078	2.29	1.87	3.34	0.75	305	43.4
USGS-27	2.15	1.19	**	0.38	0.051	0.40	0.40	0.22	(-4.0)	812	(0.4)
USGS-31	1.67	1.16	0.84	0.38	0.023	0.14	0.53	1.01	0.48	285	45.1
USGS-26	0.14	2.71	4.30	0.78	0.033	0.24	1.75	0.94	0.45	282	29.6

* The model input also included 0.28 and 0.31 dpm g^{-1} for ^{238}U and ^{232}Th in the basalt, and 1.8 and 5.4 dpm L^{-1} for ^{238}U and ^{234}U in the recharging waters, respectively. The α recoil input for the Th series nuclides equals that of ^{222}Rn multiplying by 0.9. The parenthesized values at USGS-27 is anomalous due to influence of nearby agricultural activities on the groundwater U concentration [5]. The uncertainties of the estimates come largely from estimation of the α-recoil input rates which should be good to within a factor of 2 [1].

** Values are either negative or smaller than those of ^{228}Th. In these cases, the same retardation factors were assumed for ^{232}Th and ^{228}Th and the average k_1 and k_2 values, 1.08 min^{-1} and 0.58 y^{-1} respectively, were used to calculate $R_{f,Th234}$.

Estimates of $R_{f,Ra}$ for all samples average $(1.6\pm0.9)\infty10^4$, similar to that reported by Krishnaswami et al. [1] for a number of gravel aquifers in Connecticut. Although the two aquifers have different rock types, they are all nearly saturated in dissolved oxygen, and contain relatively low concentrations of dissolved solids. For hypersaline or more reducing waters, Ra generally has higher mobility [7]. It appears that the groundwater chemistry, not the mineralogy of the aquifer rocks, mainly controls the retardation of Ra isotopes. Our estimates may reflect the typical $R_{f,Ra}$ values for the oxygenated, low-salinity groundwaters.

We have shown that the minimum desorption rate constant of Ra is 0.19 d^{-1}. Therefore, from eqn. (2), the sorption rate constant (k_1) of Ra is estimated to have a minimum value of 2.1 ± 1.2 min^{-1}, i.e., the sorption occurs on time scales of less than one minute, much faster than their transport by groundwater flow.

Th isotopes: The retardation factors of ^{228}Th (R_{fTh228}) were estimated using eqn. (5) to range mostly from 10^5 to 10^6, about two orders of magnitude higher than those of Ra isotopes. R_{fTh228} exhibits large spatial variations. Low R_{fTh228} values occur mainly in wells where we also found high ^{230}Th and ^{232}Th concentrations due possibly to colloidal association. The low R_{fTh228} values could also reflect such an association.

The retardation factors of Th isotopes are isotope-dependent: $^{232}Th \bullet {}^{230}Th > {}^{228}Th > {}^{234}Th$ (Table II). That $R_{fTh232} > R_{fTh228}$ for most of the samples suggests that the desorption rate constant of Th must be comparable to or smaller than the decay constant of ^{228}Th (0.363 y^{-1}). From eqn. (2), we estimated the sorption and desorption rate constants (k_1 and k_2) of Th to range from 0.12 to 4.1 min^{-1} and 0.1 to 2.5 y^{-1}, respectively Whereas the sorption rates of Th and Ra are comparable, the desorption of Th is about two orders slower than that of Ra.

U isotopes: Because of the long half lives of ^{238}U and ^{234}U, their R_f values are expected to be the same and estimated to be mostly in the range of 10^2–10^3, much smaller than those for Ra and Th isotopes. However, even in this oxygenated, bicarbonate-rich groundwater of INEEL, U is moderately retarded by aquifer solids. This should serve as a cautionary note to using U isotopes as a conservative tracer for groundwater dating or mixing studies.

Since most aquifers have porosities < 0.3 and rock densities ~ 2.8 g cm^{-3}, the in-situ distribution coefficients (K_d) of radionuclides are estimated to be at least an order of magnitude smaller than the values of R_f ($\bullet K$)[1], i.e., they are on the order of 10^5 for Th, 10^3 for Ra and 10^2 for U. Because R_f is site-dependent, the radionuclide migration in water-rock systems can be better understood from the in-situ K_d, rather than from the laboratory-derived K_d.

Dissolution and Precipitation

Dissolution and precipitation exhibit large spatial variations (Table II), with high rates occurring in recharge areas of the Birch Creek and Little Lost River drainages. There, the groundwater apparently is "aggressive" enough to dissolve aquifer rocks at a rate up to 800 mg L^{-1} y^{-1}, much higher than rates of <100 mg L^{-1} y^{-1} in southeastern INEEL where the groundwater is older. If the dissolution rate is assumed to be constant with time, it would take less than about one million years for the aquifer rocks to be completely weathered. However, since dissolution occurs mainly in the fractured rocks, fresh basalts of one million years old may still exist if they are not fractured. It should be noted that the above estimates represent the total-rock dissolution rates, and since >75% of the minerals in the rock are oxides of Si, Al, and Fe [6] which are mostly re-precipitated into the solid pool during dissolution, the net dissolution rates of the aquifer rock will be much smaller than the total dissolution rates as estimated above.

Precipitation occurs on the time scales of days for Th, years for Ra, and 10^2 years for U and shows large regional variations. High k_p values are generally found in areas of high dissolution rates, e.g., in recharge regions north of INEEL. High dissolution and precipitation rates, hence high weathering rates, in these areas are likely in association with the presence of abundant microfractures in aquifer rocks as suggested by the groundwater ^{222}Rn data discussed earlier.

The above estimates indicate that, for short-lived Th (^{234}Th and ^{228}Th) and Ra (^{228}Ra and ^{224}Ra) isotopes, the dissolution and precipitation rates are orders-of-magnitude lower than the rates of supply by *in-situ* production from their sorbed and dissolved parents and/or by α-recoil injection from the solid pool. This justifies us to ignore dissolution and precipitation for short-lived Th and Ra isotopes in our model. However, for long-lived U (^{234}U and ^{238}U), Th (^{230}Th and ^{232}Th), and Ra (^{226}Ra) isotopes, dissolution and precipitation have rates comparable to, or greater than, the in-situ production and/or α-recoil supply. These processes must all be taken into account in the model simulations.

Groundwater Transit Time

Estimated groundwater transit times (τ_w) range from <10 y in the recharge regions to >90 y in central INEEL, with the oldest waters occurring in the central and southeast parts of the site. For the entire Snake River Plain Aquifer, the transit time has been estimated by other methods at 200–250 y [8]. By dividing the aquifer into several compartments, Ackerman [9] showed that the travel time of regional flows in the Mud Lake compartment (which covers the INEEL area) is less than 100 y.

The spatial variation of τ_w serves to highlight the preferential flow paths in the aquifer, with flow velocity taken to be inversely related to τ_w. The results suggest two major groundwater pathways (Fig. 1). The wells ANP-6 and USGS-19 with τ_w <10 years represent the locations of recharge. The recharged water migrates from the vicinity of Birch Creek and Little Lost River via two preferential paths southward into the major aquifer. Stagnated water exists in areas southeast of the Lost River and Lemhi Ranges. A relatively young water occurs at USGS-86 in the southwestern corner of INEEL and it may originate from the Big Lost River drainage.

CONCLUSIONS

Modeling U and Th series disequilibria in groundwaters at INEEL has provided quantitative estimates for the following parameters: (1) time scales of sorption (minutes for Ra and Th), desorption (days for Ra and years for Th), and precipitation (days for Th, years for Ra, and centuries for U); (2) retardation factors due to sorption (>10^6 for ^{232}Th, ~10^4 for ^{226}Ra, and ~10^3 for ^{238}U); (3) dissolution rates of rocks (~70 to 800 mg L^{-1} y^{-1}); and (4) groundwater transit time (<10 to ~90 years). Two local north-south preferential flow pathways have been

delineated from the spatial variations in groundwater transit time. It appears that groundwater chemistry and size and density of the aquifer-rock microfractures exert an important control on retardation factors and precipitation and dissolution of radionuclides in groundwater.

This study shows that the observed decay-series disequilibria in groundwater are best explained by the presence of a sorbed pool of radionuclides which are exchangeable with their dissolved counterparts through sorption/desorption. Recognizing the role of this sorbed pool cautions us on the use of batch experiments to determine distribution coefficients of radionuclides. If freshly crushed rocks were used in such experiments, it could present artificially altered surface sorption sites. In nature, such sites would normally be formed over geological time scales. The in-situ parameters derived from the decay-series disequilibria could be used in the site-dependent performance assessment models to more realistically predict the nuclear waste migrations in the far field. They may also be used for testing and validation of the performance assessment models that are based on the laboratory-determined sorption-desorption and dissolution-precipitation parameters.

Studies of radionuclide transport in geologic systems based on naturally occurring decay-series disequilibria, such as the multiple-tracer approach of the present study, have the advantage of obtaining in-situ sorption/retardation data integrated over a range of timescales. However, a detailed characterization of the systems faces the limitation of inadequate constraints on the physical, chemical, and geological processes which control the nuclide distribution among various geochemical reservoirs. For example, our treatment of the interfacial processes of dissolution-precipitation and adsorption-desorption has left room for improvement, in the sense that bulk averages rather than individual mineral surfaces are considered. The role of colloidal transport also awaits evaluation, so do the influences of water chemistry and rock mineralogy.

ACKNOWLEDGMENTS

Work sponsored by DOE Environmental Management Science Program.

REFERENCES

1. S. Krishnaswami, W. C. Graustein, K. K. Turekian, and J. F. Dowd, Water Resour. Res. **18**, 1663-1675 (1982).
2. I. G. McKinley and W. R. Alexander, J. Contaminant Hydrology **13**, 249-259 (1993); Radiochimica Acta **74**, 263-267 (1996).
3. T. L. Ku, S. Luo, B. W. Leslie, and D. E. Hammond, in *Uranium Series Disequilibrium: Applications to Earth, Marine and Environmental Sciences*, edited by M. Ivanovich and R. S. Harmon (Clarendon Press, Oxford, 1992), pp. 631-668; Radiochim. Acta **80**, 219-223 (1998).
4. W. M. Murphy, in *Sixth EC Natural Analogue Working Group Meeting, Proceedings of an international workshop held in Santa Fe, New Mexico, USA*, edited by H. von Maravic and J. Smellie (European Commission, EUR16761, 1996), pp. 233-241.
5. S. Luo, T. L. Ku, R. Roback, M. Murrell, and T. L. McLing, Geochim. Cosmochim. Acta (in press).
6. L. L. Knobel, L. Cecil, T. S. and Wood, *U. S. Geological Survey Open-File Report* 95-748, Idaho Falls, Idaho, 1995.
7. J. G. Zukin, D. E. Hammond, T. L. Ku , and W. A. Elder, Geochim. Cosmochim. Acta **51**, 1719-1931.
8. W. W. Wood and W. H. Low, Geol. Soc. Amer. Bull. **97**, 1456-1466 (1986).
9. D. J. Ackerman, *U. S. Geological Survey Water Resources Investigations Report* 94-4257, Idaho Falls, Idaho, 1995.