Final Report to the DOE EMSP Program
Project #: DE-FG07-97ER14763
(5/1/97 - 4/30/01)

PI: Teh-Lung Ku
Dept. of Earth Sciences, University of Southern California, Los Angeles, CA 90089-0740
phone: 213-740-5826, email: rku@usc.edu

Project Title: Characterization of Contaminant Transport Using Naturally-Occurring U-Series Disequilibria

Introduction

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. Radioactive disequilibria among members of these decay-series nuclides can provide information on the rates of adsorption-desorption and transport of contaminants as well as on fluid transport and rock dissolution in a natural setting. We have developed a model of contaminant migration in the Snake River Plain Aquifer beneath the Idaho National Engineering and Environmental Laboratory (INEEL), Idaho. The model simulation was done by evaluating the retardation processes involved in the rock/water interaction. The major tasks included the determinations of: (1) the distribution of U, Th, Pa, Ra, Rn, Po and Po isotopes in groundwaters collected from 23 wells at INEEL, (2) 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 has advanced our quantitative understanding of the migration of radionuclides in groundwater as well as helped delineate major hydrogeologic features which may impact contaminant migration at the INEEL site.

Major Achievements

(1) *In-situ filtration and radioisotope-enrichment techniques for large-volume groundwater sampling and simultaneous measurements of low-level decay-series radioisotopes*

The development of an in-situ filtration-enrichment sampling system enabled us to collect radioisotopes from >1000-liter groundwater samples from 23 wells at the study site. On these samples, we measured isotopes of uranium (^{238}U and ^{234}U), thorium (^{232}Th, ^{230}Th, ^{228}Th, and ^{234}Th), radium (^{226}Ra, ^{228}Ra, and ^{224}Ra), polonium (^{210}Po), and lead (^{210}Pb). The radioisotopes were pre-concentrated in the field by passing ~1000 liters of groundwater through two cartridge filtration units (connected in series) containing MnO_2-impregnated acrylic fiber adsorbers. Smaller samples were also collected for Th, Pa and Ra concentration measurements by TIMS, and for ^{222}Rn measurements by the radon emanation method using alpha-scintillation counting. We had conducted three field sampling trips. The last field sampling was completed during September 1998.

An analytical scheme was designed to simultaneously measure the above mentioned radionuclides. The various isotopes were $\alpha/\beta/\gamma$ counted after appropriate radiochemical separation and purification procedures. A major portion of the analytical results is summarized in Table 1. Activities of ^{226}Ra, ^{228}Ra, ^{224}Ra, and ^{234}Th range from 10 to 100 dpm/m^3 and those of ^{210}Po, mostly from 1 to 10 dpm/m^3 (not shown in the table), whereas the activities of ^{232}Th, ^{230}Th, and ^{228}Th are all less than 1 dpm/m^3.

Table I. Measured decay-series isotope activities and activity ratios in groundwater at INEEL, Idaho*

Well No.	^{238}U dpm/L	^{232}Th dpm/m^3	^{226}Ra dpm/m^3	^{222}Rn dpm/L	$\frac{^{234}U}{^{238}U}$	$\frac{^{234}Th}{^{238}U}$	$\frac{^{230}Th}{^{232}Th}$	$\frac{^{228}Th}{^{232}Th}$	$\frac{^{228}Th}{^{228}Ra}$	$\frac{^{228}Ra}{^{226}Ra}$	$\frac{^{224}Ra}{^{228}Ra}$
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. 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. The data in parentheses are interpolated from the observed relationship between $^{228}Ra/^{226}Ra$ and ^{222}Rn.

(2) *Tracing the preferential flows and contaminant transport pathways*

We found similar spatial patterns of systematic variations of the activity ratios $^{234}U/^{238}U$, $^{234}Th/^{230}Th$, and $^{224}Ra/^{228}Ra$ (Fig. 1). The patterns allowed us to delineate preferential flow pathways. They reflect aging of groundwater, degree of rock weathering, and intensity of nuclide flux due to α-recoil in the aquifer, as briefly explained below.

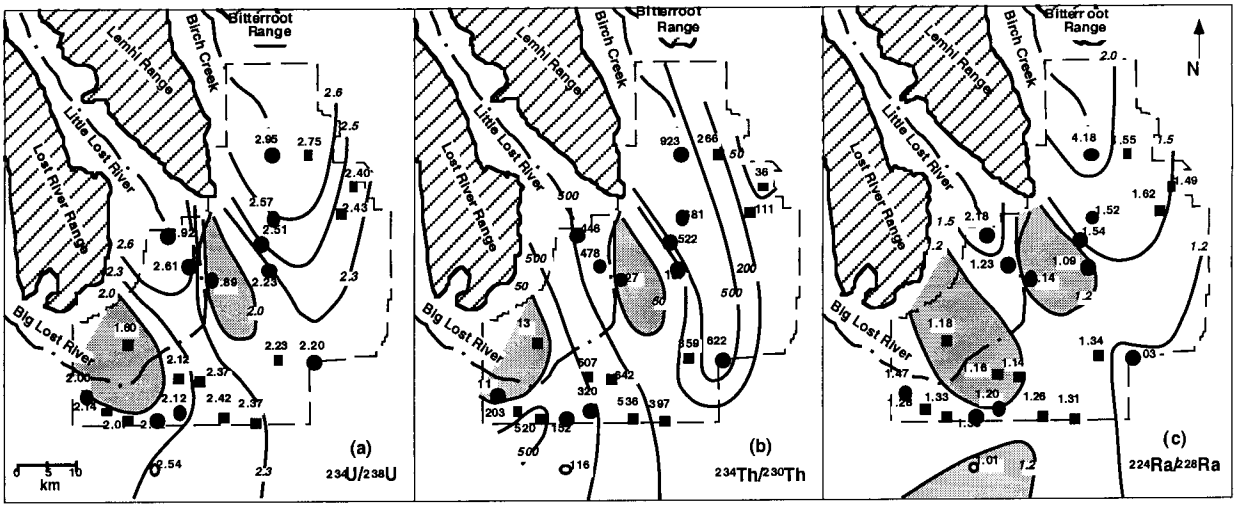

Fig. 1. Distributions of (a) $^{234}U/^{238}U$, (b) $^{234}Th/^{230}Th$, and (c) $^{224}Ra/^{228}Ra$ activity ratios in INEEL groundwater, all showing southward decreases along two preferential flow paths with minimum values occurring just south of Lost River and Lemhi Ranges. The general similarities among the three plots reflect aging of groundwater, degree of rock weathering, and intensity of α-recoil radionuclide flux in the aquifer. "Low" values inside shaded areas encircled (or semi-encircled) by contour lines.

$^{234}U/^{238}U$

Fig. 1a shows that the water entering the aquifer has an initial $^{234}U/^{238}U$ activity ratio of ~3. Fast-flowing groundwater has less time to leach aquifer solids, thus exhibiting a smaller decrease in $^{234}U/^{238}U$. Based on this notion, two southward preferential flows into the Snake River Plain aquifer can be identified from the $^{234}U/^{238}U$ data: one from the Birch Creek and the other from the Little Lost River (Fig. 1a). The low $^{234}U/^{238}U$ ratios in areas south of the Lost River Range and the Lemhi Range reflect stagnation of water movement. Similar flow patterns have been deduced from $^{87}Sr/^{86}Sr$. Upwelling of geothermal water may occur in the low $^{234}U/^{238}U$ areas but its effect on the $^{234}U/^{238}U$ pattern appears insignificant as geothermal waters have U concentrations typically 1 to 2 orders lower than ordinary ground waters.

Our data do not show a clear linear correlation between $^{234}U/^{238}U$ and $[^{238}U]^{-1}$. This observation, along with the finding that both ^{238}U concentrations and $^{234}U/^{238}U$ ratios are significantly lower in the stagnated groundwaters than in the recharging waters, further points to water-rock interactions as an important control on groundwater $^{234}U/^{238}U$. The lowering of ^{238}U concentrations away from the recharge areas suggests a net removal of U onto aquifer rocks through precipitation (which, unlike dissolution, should not affect ratio $^{234}U/^{238}U$.)

$^{234}Th/^{230}Th$ and $^{228}Th/^{232}Th$

Unlike ^{230}Th and ^{232}Th, short-lived ^{234}Th and ^{228}Th show little variations because their activities, being largely supported by the decay of their more soluble parents ^{238}U and ^{228}Ra, are relatively insensitive to dissolution and precipitation. Thus the high $^{234}Th/^{230}Th$ ratios occurring within the major flow paths largely reflect a decrease in ^{230}Th. This could result from precipitation of ^{230}Th along flow paths, as precipitation tends to lower the concentrations of long-lived ^{230}Th and ^{232}Th more than those of shorter-lived ^{234}Th and ^{228}Th. The higher $^{234}Th/^{230}Th$ and $^{228}Th/^{232}Th$ ratios in recharging waters, therefore, likely result from mineral precipitation caused by interaction of young groundwaters with rocks.

$^{224}Ra/^{228}Ra$:

Similar to ^{222}Rn, short-lived ^{224}Ra is supplied to groundwater mainly by α recoil. The systematic decrease of $^{224}Ra/^{228}Ra$ along the flow paths (Fig. 1c) is attributable to a decrease in the α-recoil rate, or fracture density, of the aquifer rocks.

(3) *U/Th series disequilibria as natural analogs for quantitative information on water-rock interactions and contaminant transport*

The observed U/Th series disequilibria enable quantification of the groundwater residence time, rock dissolution rates, and rates of sorption, desorption and precipitation (co-precipitation) of radionuclides in the groundwater. The results indicate that rocks in contact with newly-recharged groundwaters in the northern part of INEEL dissolve at a rate of ~800 mg/L/y, whereas rocks in the southern part in contact with older groundwaters dissolve at ~70 mg/L/y. Precipitation occurs on time scales of the order of hours-to-days for thorium, months for radium, and years for uranium. Subsurface water residence times range from ~1 year in the north to ~100 years in the central and southwestern parts of INEEL. Based on these residence time estimates, we conclude that two preferential flows occur in the INEEL area, with one flow originating from the Birch Creek and the other from the Little Lost River valleys, both flowing southward into the Snake River Aquifer.

We have estimated the degree of retardation due to rock-water interaction in the groundwater system at INEEL by modeling the observed radioactive disequilibria. Our model results indicate that adsorption of radium by the aquifer solids at the site takes place on time scales of a few tenths of a second to several seconds, similar to those of thorium. The desorption times, on the other hand, are several days for radium and several years for thorium. Based on these sorption-desorption rate characteristics, we estimated that the in-situ retardation factors (i.e., the ratio of flow rates of fluid to those of dissolved radionuclides) are of the order of 10^6 for ^{230}Th, 10^4 for ^{226}Ra, and 10^3 for ^{238}U. The model predicts that the sorbed radionuclides on solids, which are exchangeable with their dissolved counterparts through sorption and desorption, play an important role in affecting the decay-series disequilibrium in groundwater systems. The model also indicates that the major source of ^{222}Rn in groundwater in the study area is the decay of ^{226}Ra sorbed on aquifer solid surface, rather than the direct alpha recoil from the solid ^{226}Ra pool, as previously thought.

The retardation-factor estimates that we have derived are of value to our understanding of the disposal and migratory behavior of radioactive wastes at INEEL. The estimates allow us to delineate a rather large range of migration rates for possible contaminants in groundwater at the site and suggest that three groups of wastes can be identified in terms of their mobility. The migration of radionuclides with high ionic potential (readily hydrolyzed) such as thorium and lanthanide fission products is heavily retarded. The degree of retardation for alkali- and earth alkali-radionuclides (e.g., ^{133}Ba, ^{90}Sr, and ^{137}Cs), is such that these nuclides are unlikely to be transported far away from the contaminated areas. Uranium, and perhaps some transuranic radionuclides, have a relatively high degree of mobility in the aquifers we have studied.

Publications and meeting presentations on the work supported under DE-FG07-97ER14763

1. Ku, T. L., Luo, S., Leslie, B. W., and Hammond, D. E., "Assessing In-Situ Radionuclide Migration from Natural Analog Studies: Response to McKinley and Alexander (1996)," *Radiochimica Acta*, **80**, 219-223, 1998.

2. Luo, S., Ku, T. L., Roback, R., Murrell, M., and McLing, T., "Uranium-Series Disequilibria In Groundwater: Assessing Radio-Nuclide Migration," 9th International Conference on Isotope Geology, Cosmochemistry and Geochronology, Aug. 21-26, Beijing, 1998, *Chinese Science Bulletin, vol. 43 Supplement,* p. 86

3. Roback, Robert C., Murrell, Michael, Nunn, Andy, Johnson, Thomas, McLing Travis, Luo, Shangde and Ku, Richard, "Groundwater Mixing, Flowpaths and Water/Rock Interaction at INEEL: Evidence from Uranium Isotopes," *Geological Society of America, Abstracts with Programs, v. 29, no. 6,* 1997.

4. Luo, S., Ku, T. L., Roback, R., Murrell, M., and McLing, T., "Assessing In-Situ Radionuclide Transport Based on Uranium-Series Disequilibrium in Groundwater", Fall AGU Meeting, Dec. 6-10, 1998, San Francisco, *EOS Trans. Amer. Geophys. Un.* 79 F354, 1998.

5. Roback, R. C., Murrell, M. T., Nunn, A., Luo, S., Ku, T. L., and McLing, T., "Uranium and Thorium Series Isotopes in Fractured Rocks at the INEEL", Fall AGU Meeting, Dec. 6-10, 1998, San Francisco, *EOS Trans. Amer. Geophys. Un.* 79 F343, 1998.

6. Johnson, T. M, Roback, R. C., McLing, T. L., Bullen, T. D., DePoalo, D. J., Murrell, M. T., Hunt, R., Smith, R. M., Doughty, C., Ku, T-L., "Radiogenic Isotope Ratios in Groundwater: "Well Behaved" Natural Tracers", *manuscript,* 1999.

7. Luo, S., Ku, T. L., Roback, R., Murrell, M., and McLing, T., "In-situ Radionuclide Transport and Preferential Groundwater Flows at INEEL (Idaho): Decay-Series Disequilibrium Studies" *Geochim. Cosmochim. Acta*, **64**, 867-881, 2000.

8. Luo, S., Ku, T. L., Roback, R., Murrell, M., and McLing, T., "Decay-Series Disequilibrium Study of In-Situ, Long-Term Radionuclide Transport in Water-Rock Systems" *Symposium of Scientific Basis for Nuclear Waste Management XXIII, Materials Research Society*, vol. **608**, pp. 217-224.

9. Roback, R. C., Murrell, M. T., Ku, T. L., Luo, S., Johnson, T.M, and McLing, T., "Groundwater evolution and preferential flow pathways in Snake River Plain Aquifer in the Vicinity of the INEEL: Constraints from $^{234}U/^{238}U$ Isotope Ratios", *Bull Geol. Soc. Am,* in press, 2001 .