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ABSTRACT

Morin, K.A., Cherry, J.A., Davé, N.K., Lim, T.P. and Vivyurka, A.J., 1988. Migration of acidic groundwater seepage from uranium-tailings impoundments, 2. Geochemical behavior of radionuclides in groundwater. *J. Contam. Hydrol.*, 2: 305–322.

In this second paper of a series on groundwater seepage from uranium tailings, the general geochemical behavior of radionuclides is described and then applied to data from the field site, Seepage Area A of the Nordic Main impoundment near Elliot Lake, Ontario. The delineation of radionuclide behavior requires (1) the calculation of total element concentration by the summation of concentrations of each element's isotopes (the isotopic concentrations are calculated from the isotopes' radioactivities), (2) the evaluation of solid–liquid interactions using total element concentrations, and (3), for particular isotopes, the evaluation of the extent to which parental geochemical behavior causes a deviation in the isotope's behavior from that of its total element. A computerized speciation program, WATRAD, is used to evaluate aqueous complexation and mineral saturation indices of radium, actinium, thorium, and uranium. Data from Seepage Area A on isotopes of these four elements plus ^{210}Pb show that the geochemical behavior of radionuclides can be best defined on an individual isotopic basis rather than on an elemental basis.

1. INTRODUCTION

The first paper of this series (Morin et al., 1988) described a field study of acidic and pH-neutral uranium-tailings seepage at the Nordic Main tailings area near Elliot Lake, Ontario, and developed a conceptual model for contaminant migration and behavior. Major ions, minor ions, metals, and stable isotopes were examined through the model. This second paper specifically addresses the geochemical behavior of radionuclides, particularly isotopes of radium, actinium, thorium, and uranium. Radionuclides are examined in detail as part of this series because: (1) they are a special characteristic of uranium-

tailings seepage; (2) radionuclide toxicity can be significant at less than part-per-trillion levels; (3) geochemical behavior of radionuclides is more complex than that of many ions and metals; and (4) there is a general lack of field evaluations of radionuclide migration in groundwater.

The geochemical behavior of radionuclides is complex for several reasons. First, the behavior depends in part on the radionuclide's radioactivity, commonly expressed as BqL^{-1} or $pCiL^{-1}$ (1 $pCiL^{-1} = 0.037$ BqL^{-1}). A nuclide's radioactivity will simply be called "activity" in this paper and, thus, should not be confused with chemical activity. Second, the behavior depends in part on the radionuclide's chemical concentration, such as in $molesL^{-1}$, which can be calculated from activity and half-life:

$$moles\,L^{-1} = 10^{-23.62}\,(Bq\,L^{-1})\,(\text{half-life in seconds}) \tag{1}$$

Third, the behavior depends in part on the respective element's total concentration, representing a summation of each isotope's concentration calculated from eqn. (1). The sorptive behavior of radium, for example, is regulated by the total concentration of radium, which is a summation of the concentrations of ^{226}Ra, ^{223}Ra, ^{228}Ra, and ^{224}Ra (Figs. 1–3). Fourth, the behavior depends in part on the behavior of the parent radionuclide, and the behavior of the parent is also dependent on the previous three factors. Additionally, if a parent radionuclide on the solid-phase decays by alpha-particle emission to the daughter, then the daughter may be ejected into solution by the force of the emission. This process is commonly called "alpha recoil" (e.g., Kronfeld, 1974; Fleischer, 1982). A hypothetical example is presented to illustrate the complexities.

A hypothetical groundwater contains three isotopes of element A: A_1, A_2 and A_3 (Table 1). All three isotopes have assigned activities of 1 BqL^{-1}, although their molar concentrations are different because of the differences in half-lives. For geochemical equilibrium-based processes such as sorption and mineral precipitation-dissolution, the driving force towards equilibrium is a function of the total concentration of A. The total concentration of A in this case is
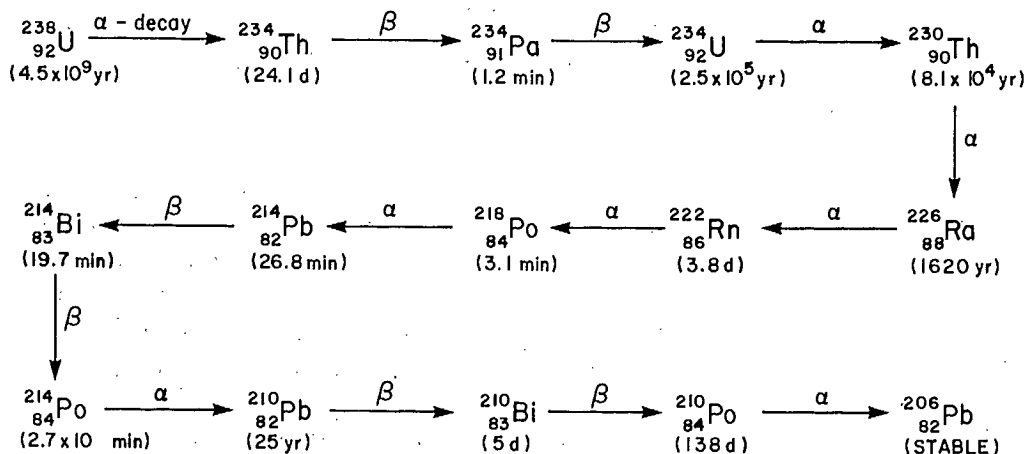
$^{238}_{92}U \xrightarrow{\;\alpha - decay\;} {}^{234}_{90}Th \xrightarrow{\;\beta\;} {}^{234}_{91}Pa \xrightarrow{\;\beta\;} {}^{234}_{92}U \xrightarrow{\;\alpha\;} {}^{230}_{90}Th$
$(4.5 \times 10^9 yr) \quad (24.1\,d) \quad (1.2\,min) \quad (2.5 \times 10^5 yr) \quad (8.1 \times 10^4 yr)$

$\downarrow \alpha$

$^{214}_{83}Bi \xleftarrow{\;\beta\;} {}^{214}_{82}Pb \xleftarrow{\;\alpha\;} {}^{218}_{84}Po \xleftarrow{\;\alpha\;} {}^{222}_{86}Rn \xleftarrow{\;\alpha\;} {}^{226}_{88}Ra$
$(19.7\,min) \quad (26.8\,min) \quad (3.1\,min) \quad (3.8\,d) \quad (1620\,yr)$

$\downarrow \beta$

$^{214}_{84}Po \xrightarrow{\;\alpha\;} {}^{210}_{82}Pb \xrightarrow{\;\beta\;} {}^{210}_{83}Bi \xrightarrow{\;\beta\;} {}^{210}_{84}Po \xrightarrow{\;\alpha\;} {}^{206}_{82}Pb$
$(2.7 \times 10\,min) \quad (25\,yr) \quad (5\,d) \quad (138\,d) \quad (STABLE)$

Fig. 1. The uranium-238 decay series: isotopes, type of decay (alpha, beta), and approximate half-life.

$$^{235}_{92}U \xrightarrow{\alpha} {}^{231}_{90}Th \xrightarrow{\beta} {}^{231}_{91}Pa \xrightarrow{\alpha} {}^{227}_{89}Ac \xrightarrow{\beta} {}^{227}_{90}Th$$
(7.1×10⁸ yr) (25.6 hr) (3.4×10⁴ yr) (27.7 yr) (18.6 d)

$$\downarrow \alpha$$

$$^{211}_{83}Bi \xleftarrow{\beta} {}^{211}_{82}Pb \xleftarrow{\alpha} {}^{215}_{84}Po \xleftarrow{\alpha} {}^{219}_{86}Rn \xleftarrow{\alpha} {}^{223}_{88}Ra$$
(2.2 min) (36 min) (1.8×10⁻³ sec) (3.9 sec) (11.2 d)

$$\downarrow \alpha$$

$$^{207}_{81}Tl \xrightarrow{\beta} {}^{207}_{82}Pb$$
(4.8 min) (STABLE)
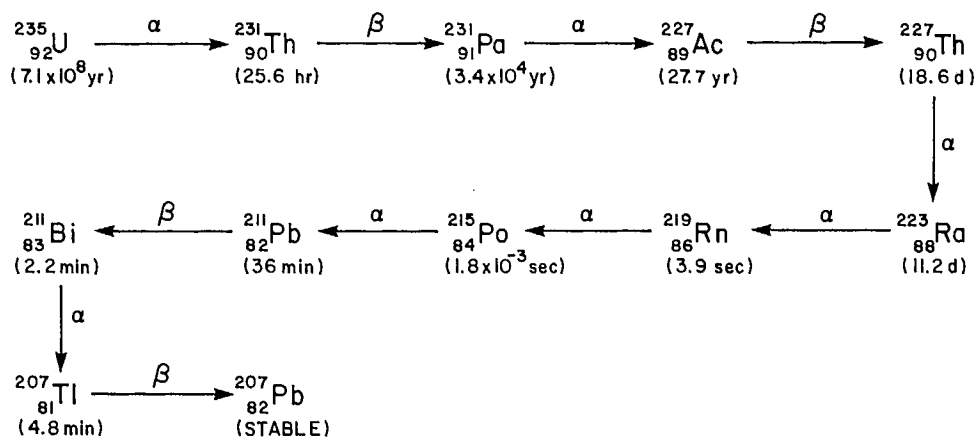
Fig. 2. The uranium-235 decay series.

$7.6 \times 10^{-11} M$ or, essentially, the concentration of the longest-lived radionuclide, A_3. This observation implies that: (1) an order-of-magnitude change in A_3 would force the regulating geochemical process to re-establish equilibrium; (2) an order-of-magnitude change in A_1 would provide little or no driving force for the regulating process because the equilibrium established by A_3 is not significantly disturbed; (3) concentrations and activities of A_1 can vary widely along a flow path whereas changes in A_3 could be moderated by a regulating solid–liquid interaction; and (4) removal of aqueous A_3 by solid–liquid interactions would also remove some aqueous A_1 and A_2 as governed by isotopic-fractionation effects, which are apparently not defined for most radionuclides. A_2 represents an intermediate case between A_1 and A_3 for all above implications.

Now the effects of parent radionuclides will be added to the hypothetical example. The parent of A_1 is P_1 and the grandparent is G_1, and similarly there is P_2 and G_2 for A_2 and P_3 and G_3 for A_3 (Table 1). If P_1 has a much longer half-life than P_3, then the concentration of P_1 will establish the solid–liquid interactions of element P and the behavior of A_1 will in some way reflect the behavior of P_1. If P_1 decay is by alpha emission, the behavior of A_1 may also be modified by
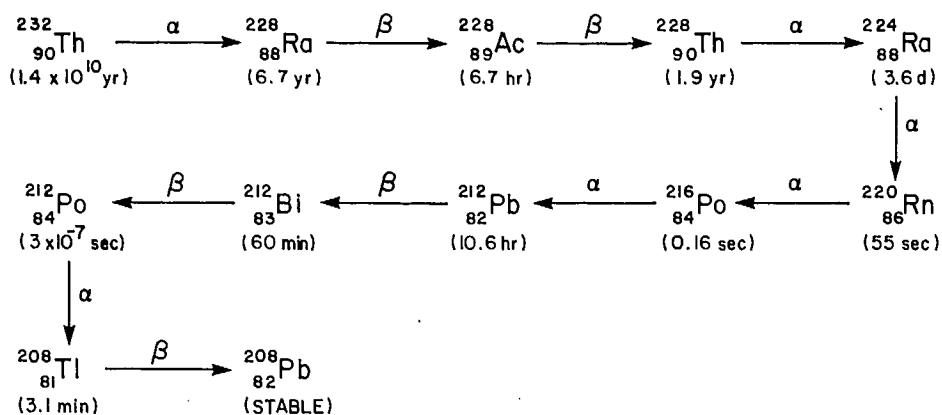
$$^{232}_{90}Th \xrightarrow{\alpha} {}^{228}_{88}Ra \xrightarrow{\beta} {}^{228}_{89}Ac \xrightarrow{\beta} {}^{228}_{90}Th \xrightarrow{\alpha} {}^{224}_{88}Ra$$
(1.4×10¹⁰ yr) (6.7 yr) (6.7 hr) (1.9 yr) (3.6 d)

$$\downarrow \alpha$$

$$^{212}_{84}Po \xleftarrow{\beta} {}^{212}_{83}Bi \xleftarrow{\beta} {}^{212}_{82}Pb \xleftarrow{\alpha} {}^{216}_{84}Po \xleftarrow{\alpha} {}^{220}_{86}Rn$$
(3×10⁻⁷ sec) (60 min) (10.6 hr) (0.16 sec) (55 sec)

$$\downarrow \alpha$$

$$^{208}_{81}Tl \xrightarrow{\beta} {}^{208}_{82}Pb$$
(3.1 min) (STABLE)

Fig. 3. The thorium-232 decay series.

TABLE 1

Hypothetical characteristics of radio-isotopes of element A

	Half-life (s)	Hypothetical activity (Bq L^{-1})	Concentration (molar) from eqn. (1)
A$_1$	86,400 (1 day)	1	2.1 × 10^{-19}
A$_2$	3.15 × 10^9 (10^2 yr)	1	7.6 × 10^{-15}
A$_3$	3.15 × 10^{13} (10^6 yr)	1	7.6 × 10^{-11}

	Isotope	Parent	Grandparent
	A$_1$	P$_1$	G$_1$
	A$_2$	P$_2$	G$_2$
	A$_3$	P$_3$	G$_3$

alpha recoil off the solid phase. On the other hand, if the half-life of P$_3$ is very short (e.g., less than one second), then P$_3$ does not exist long enough to be significantly affected by most geochemical processes. Consequently, the behavior of A$_3$ will reflect the behavior of G$_3$ instead of P$_3$ if G$_3$ has a relatively long half-life. The geochemical behavior of an unmeasured intermediate such as P$_3$ can sometimes be examined by determining A$_3$/G$_3$ ratios from measurements along a flow path. For instance, if P$_3$ is a gas and the A$_3$/G$_3$ ratio decreases along a flow path, one possible interpretation is that P$_3$ gas is progressively lost from solution.

The preceding hypothetical example shows the formidable problem of understanding radionuclide behavior in groundwater. Simulation of the general scenario has apparently not been accomplished because of the large amount of required data, computer code, and execution time. However, many simulations of scenarios with simplifying assumptions exist (e.g., Lester et al., 1975; Rasmuson and Neretnieks, 1986).

Despite the complexity of combined controls on behavior, the general behavior of radionuclides can be assessed by using the following procedures. First, aqueous radioactivities and concentrations of radionuclides along a flow path are examined. Second, the behavior of short-lived isotopes are compared to that of the long-lived isotopes which may be regulated by equilibrium-based reactions. Third, total concentrations are used to determine potential solid–liquid interactions. Fourth, various ancestor/descendant ratios are calculated along the flowpath in order to assess possible behavior of unexamined intermediate (if present) radionuclides and to determine reasons for deviations of individual isotope behavior from the behavior of the element. These procedures are used in this paper with data from the centerline of the acidic plume in Seepage Area A.

2. WATER CHEMISTRY

Water samples for radionuclide analyses were taken from piezometers in Area A by the techniques outlined in the earlier paper (Morin et al., 1988).

Analytical precision reported by laboratories was $\pm 20\,\text{mBq}\,\text{L}^{-1}$. Several laboratories analyzed replicates from a few piezometers and comparison of results indicate an agreement often within a factor of 2 (Morin, 1983). However, a few replicate analyses differed by up to an extreme of one order-of-magnitude and, in these cases, the results of a third replicate when available or the results of previous and subsequent years determined which value was accepted as correct. In any case, analytical results of radionuclide concentrations typically include a larger overall error (larger standard deviation in precision and accuracy) than those of major ions.

Some results are plotted in Fig. 4. However, in order to more easily discuss and evaluate radionuclide behavior along the centerline of the plume, a composite of measured radionuclide activities and concentrations is presented in Table 2, derived from table E7 of Morin (1983).

The ^{210}Pb profile through the inner core and neutralization zone (Table 2) shows generally decreasing activities. Because ^{210}Pb comprises approximately $10^{-7}\%$ of total lead in Area A waters, the geochemical behavior of this isotope may not closely parallel that of total lead. However, total lead concentrations throughout Area A remain close to or below detection limit and, thus, a clear geochemical behavior cannot be discerned. Consequently, ^{210}Pb will only be used in this paper as an indicator of the general behavior of the lower section of the ^{238}U decay series (Fig. 1).

Total natural radium is comprised of the 226, 223, 228, and 224 isotopes (Figs. 1–3). Radium-226 profiles along the centerplane (Fig. 4) and the centerline (Table 2) indicate a decrease of approximately one order-of-magnitude in activity with a further decrease with distance to a background level of 110 mBq L^{-1} (3 pCi L^{-1}). Because ^{226}Ra levels emanating from the source area are decreasing with time, clear forward movement of the ^{226}Ra front is not obvious (Fig. 4). Radium-223 rivals ^{226}Ra in activity, but is less than 0.01% of ^{226}Ra on a molar scale. The ^{223}Ra trend in 1982 (Table 2) is similar to that of ^{226}Ra, but the decrease in activity is only about a factor of 1.9 to M16 whereas ^{226}Ra decreases by a factor of about 2.5. Activities of ^{228}Ra and ^{224}Ra were not measured, but they are at levels of about 200 mBq L^{-1} if approximate isotopic equilibrium with their parents (^{232}Th and ^{228}Th, respectively) is assumed. At these levels, ^{228}Ra and ^{224}Ra would be less than 0.02% and 0.00003% of ^{226}Ra concentrations. Therefore, the concentration of ^{226}Ra essentially represents total radium, and it is apparent that ^{223}Ra deviates from the trend of total radium along the centerline.

Actinium, represented by ^{227}Ac and ^{228}Ac in the natural decay series, is rarely measured in natural waters (Morin, 1983), causing its general behavior to be less understood than many radionuclides. In this study, ^{227}Ac was found to have the second highest activity of all measured radionuclides and ^{227}Ac activity was observed to decrease by a factor of 4.4 through the neutralization zone to piezometer M17. Although ^{228}Ac was not measured, it is at a level of about 200 mBq L^{-1} based on the general activities of its grandparent (^{232}Th) and daughter (^{228}Th). As a result, ^{228}Ac concentrations are probably less than $10^{-4}\%$ of ^{227}Ac, which justifies the use of ^{227}Ac as total actinium.

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pCi/L   RADIUM-226 (1979)
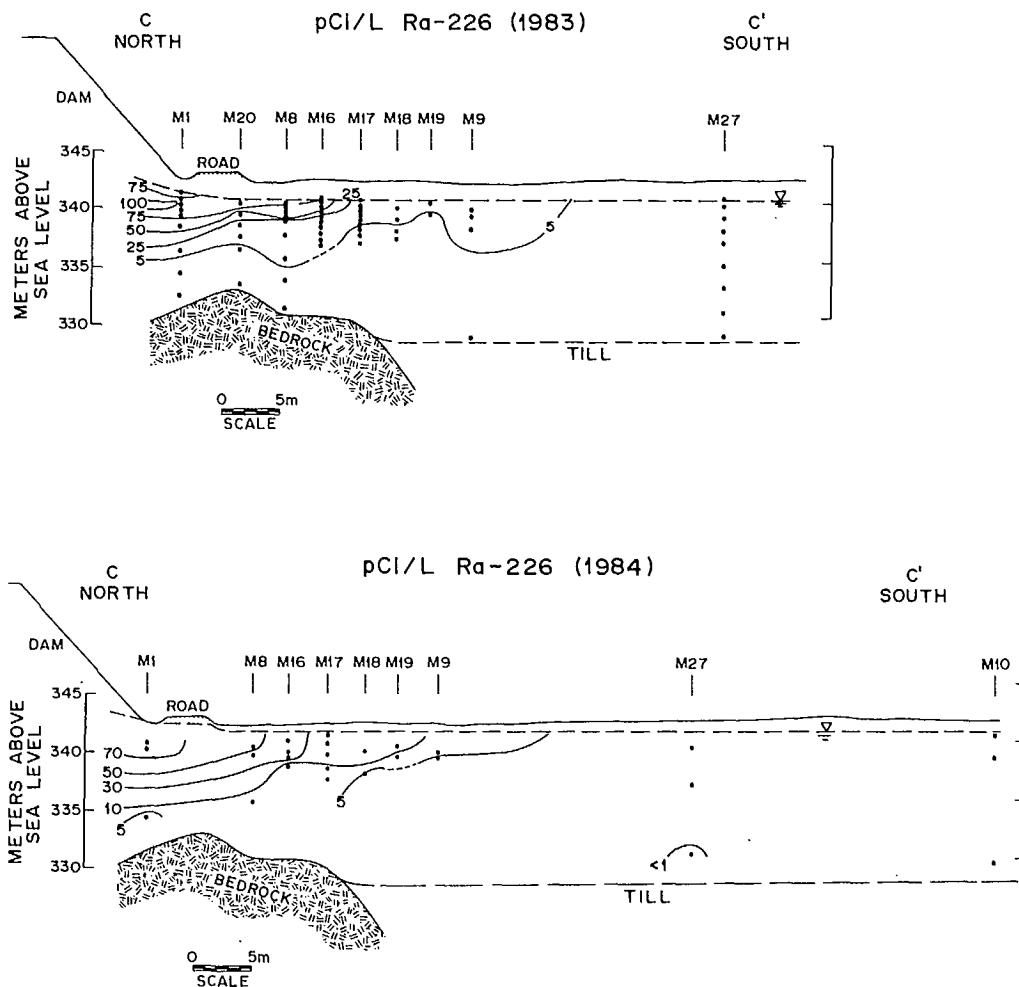

pCi/L   RADIUM-226 (1980)

pCi/L   RADIUM-226 (1981)
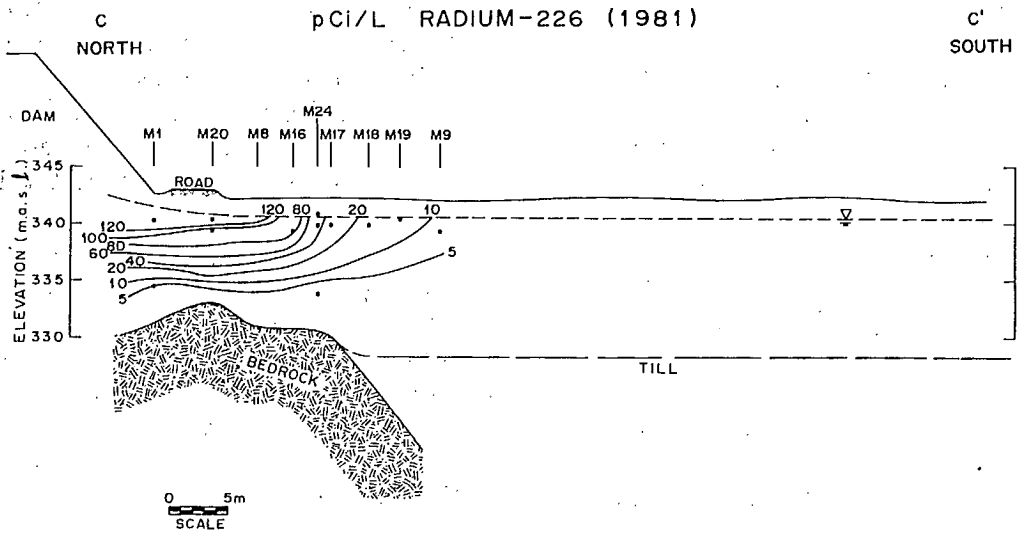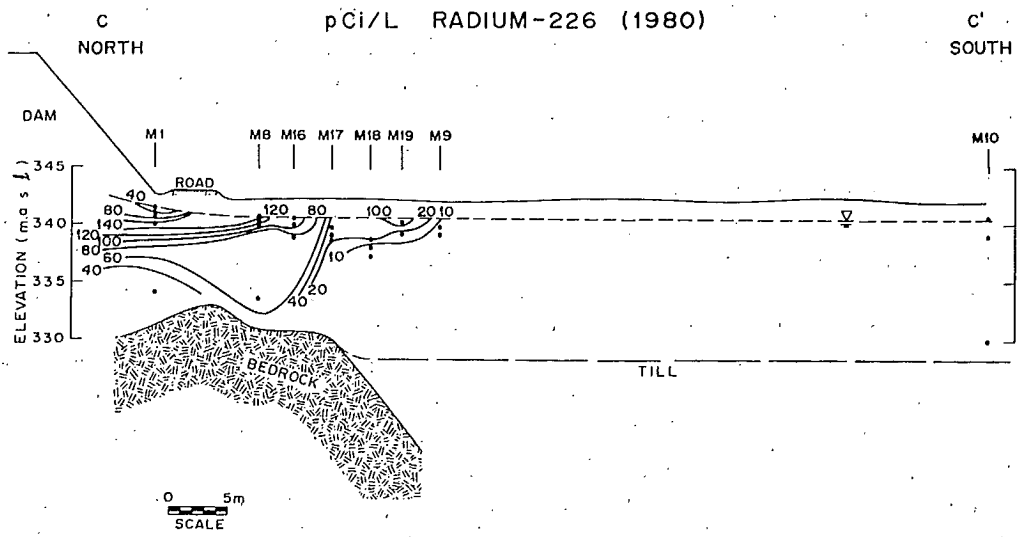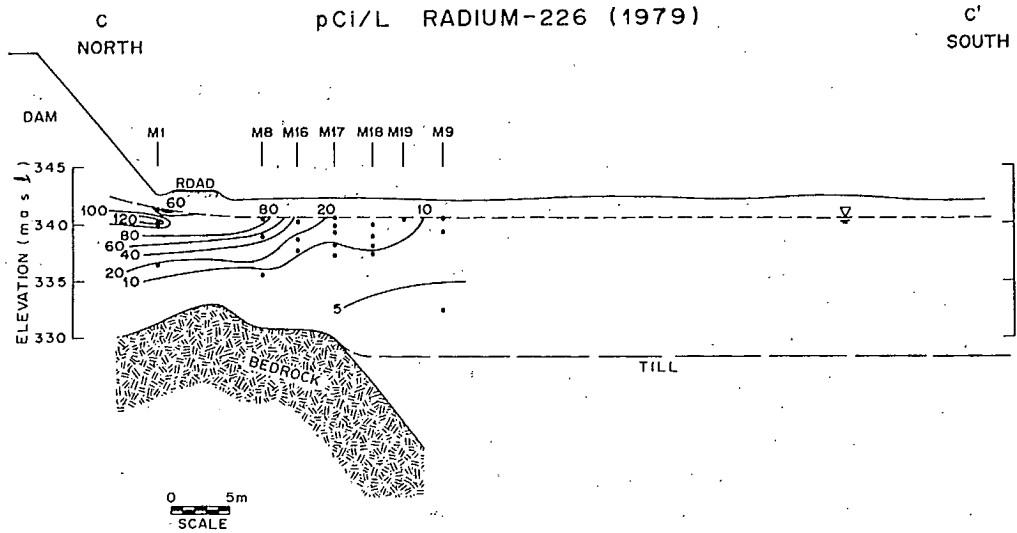
Fig. 4. Yearly centerplane profiles for radium-226.

Naturally occurring thorium isotopes are 227, 228, 230, 231, 232, and 234. Thorium-227 (Table 2) has the highest measured activity in Area A waters and, with [227]Ac and [223]Ra data, indicate the [235]U decay series is significant in Area A waters compared to natural gross occurrence in the earth's crust. Activities of [227]Th decrease by a factor of about 6.6 through the neutralization zone to M17. The trend in activities of [228]Th is not clear (Table 2), but in a general manner appears to follow the trend of its ancestor, [232]Th. Thorium-230 displays a general decrease in activity by a factor of about 7–12 to M17 and the anomalously high value at M19 may be erroneous. Thorium-231 was not measured in Area A, but it may be at levels up to $20,000\,\mathrm{mBq\,L^{-1}}$ based on the [227]Ac granddaughter. Thorium-232 appears to generally increase then decrease through the neutralization zone for an overall decrease by a factor of 3–6. Thorium-234 was not measured in Area A, but is expected at levels of $6000\text{–}300\,\mathrm{mBq\,L^{-1}}$ based on its parent, [238]U. Because [232]Th has an extremely long half-life, its concentration represents total thorium in Area A despite the wide range of activities for

Measured radionuclide data from the plume centerline in Area A (values in mBq L^{-1} unless marked as molal; reported analytical precision ± 20 mBq L^{-1}; values > 100 are rounded to the nearest 10 mBq L^{-1}).

	M1	M20	M8	M16	M17	M18	M19	
Distance from M1 (m)	0	4.8	8.7	11.8	15.0	17.7	20.8	
Field pH	4.40	4.61	4.90	4.98	4.86	5.65	5.50	(1980 data)
	4.24	4.60	5.18	5.68	5.43	5.21	5.33	(1982)
Pb-210	520	–	59	93	37	–	19	(1980)
	100('82)	300	110	< 37	74	–	–	(1981)
Ra-223	3070	2670	2300	1630	–	–	–	(1982)
Ra-226	5930	–	5150	2780	1040	740	110	(1980)
			(For 1980 Ra-226 data, M9 has an activity of 370)					
	3850	3520	2560	1520	850	590('81)	590('81)	(1982)
Ac-227	11820	8150	7370	3960	2670	–	–	(1982)
Th-227	22220	15000	10000	5440	3370	–	–	(1982)
Th-228	130	–	190	93	< 19	< 19	–	(1980)
	< 190('82)	190	–	190	260	–	–	(1981)
Th-230	1370	–	190	130	110	< 19	1260[4]	(1980)
	1330	520	140	190	190	–	–	(1982)
Th-232	210	–	290	< 19	44	< 19	74	(1980)
	< 190('82)	37	190	220	74	–	–	(1981)
Total Th(m)[1]	2.22E−7	–	3.06E−7	< 2.01E−8	4.64E−8	< 2.01E−8	7.81E−8	(1980)
Total Th(m)[2]	2.32E−7	–	3.02E−7	4.14E−7	4.74E−8	–	7.76E−8	(1980)
U-234	7570	–	4220	3040	910	–	550	(1980)
U-238	6170	–	2000	930	300	–	140	(1980)
Total U(m)[3]	2.07E−6	–	6.72E−7	3.12E−7	1.01E−7	–	4.73E−8	(1980)
Total U(m)[2]	2.07E−6	–	6.81E−7	3.11E−7	1.01E−7	< 8.40E−10	4.62E−8	(1980)
	3.57E−5	5.88E − 6	3.36E−6	1.26E−6	1.26E−6	1.39E−8('81)	–	(1982)

[1] = calculated from ^{232}Th.

[2] = measured.

[3] = calculated from ^{238}U.

[4] = considered erroneous.

For conversion: atoms L^{-1} = 1.44 (Bq L^{-1}) (half-life in seconds); disintegrations minute^{-1} L^{-1} = 60 (Bq L^{-1}); picoCuries L^{-1} = 27 (Bq L^{-1}); moles L^{-1} = (half-life in seconds) $(10^{-23.62})$ (Bq L^{-1}).

all thorium isotopes. For samples with both measured total thorium concentration and ^{232}Th activity in 1980 (Table 2), calculations indicate that ^{232}Th concentrations often equal total thorium within analytical accuracy. However, it is clear that isotopes other than 232 do not display identical trends in aqueous activity along the centerline.

Naturally occurring uranium is composed of ^{238}U, ^{234}U, and ^{235}U. Uranium-238 exists at relatively high levels in the inner core and decreases by a factor of about 44 through the neutralization zone to M19 (Table 2). Similarly, ^{234}U is relatively high in activity in the inner core with a subsequent decrease by a factor of about 14. It is interesting to note that the ^{234}U/^{238}U activity ratio changes from 1.2 to 3.9 over a distance of about 21 m, which represents a temporal spacing of about 24 days. Other studies which have reported ratios from 0.71 to 30 are summarized in Morin (1983). The significant shift in the ^{234}U/^{238}U ratio, like the variation in stable isotopes (Morin et al., 1988), attests to the high geochemical reactivity of Seepage Area A groundwater.

Uranium-235 was not measured, but may comprise approximately 5% of total uranium on a molar scale if it occurs at activities close to those of ^{227}Th and ^{227}Ac. These activities and concentrations represent strong enrichment of the ^{235}U series in Area A waters over natural gross abundances, which would overcome the common dismissal of the ^{235}U series as unimportant because of natural abundance (e.g., Levinson and Coetzee, 1978).

For 1980 data (Table 2), measured total uranium is in agreement with total uranium calculated from ^{238}U, indicating ^{238}U generally accounts for all uranium on a molar basis. However, the ^{234}U data indicate there are significant differences in the geochemical behavior of uranium isotopes.

3. SPECIATION AND SOLUBILITY CONTROLS

3.1 Introduction

Studies on sorption, co-precipitation, and solubility of radionuclides often ignore effects of complexation, which is inappropriate because the amount of the free ion in solution is sometimes orders-of-magnitude less than the concentrations of complexes and ion pairs (Morin, 1983). For solubility calculations, the result of speciation is lower saturation indices than would be calculated from total concentrations. For sorption and co-precipitation, the result of speciation is that the observed geochemical behavior of a radionuclide can properly be attributed to the dominant species rather than to the assumed dominant free cation. Therefore, to assist in the accurate explanation of radionuclide behavior, the radionuclides should be speciated and mineral saturation indices can then be calculated. Nevertheless, some caution must be used with mineral saturation indices because nucleation and precipitation of radionuclide minerals at very low concentrations (thereby producing very small crystals with anomalously high solubilities) may require significant supersaturation and may not always be kinetically feasible.

3.2 Thermodynamic database and the speciation program, WATRAD

In order to calculate radionuclide speciation as reliably as possible, thermodynamic data for many aqueous complexes and ion pairs of radium, actinium, thorium, and uranium were compiled (appendix D, Morin, 1983). For radium (6 aqueous species and 8 minerals), barium data were substituted for several aqueous species and minerals because of the lack of radium data. As a result, radium speciation is only suggestive of possible radium behavior. For actinium (17 species and 8 minerals), several lanthanum complexes and minerals were used, making actinium speciation only suggestive. The core of the thorium database (35 species and 9 minerals) was taken from Langmuir and Herman (1980) and the core of the uranium database (53 species and 38 minerals) was taken from Langmuir (1978) and Hemingway (1982). Enthalpy data were available for most species and minerals, except actinium-lanthanum, and the van't Hoff Equation with constant enthalpy with temperature was used to approximate temperature changes in equilibrium constants.

The data for the radionuclides were coded into a Fortran computer program entitled WATRAD (WATer-borne RADionuclides). WATRAD uses the Continuous-Fraction method for speciation, using a more efficient version where possible (Morin, 1985), and logarithmic functions are used to minimize instability from concentration oscillations ranging over 30 orders of magnitude. The Davies Equation was used to calculate chemical activity coefficients; however, the accuracy of calculations at relatively high ionic strengths for valence-4 species (e.g. Th^{4+}) is probably poor. In light of limitations of data and computation, WATRAD results do not warrant strict interpretation. WATRAD is 90 kbytes in size and has been used on microcomputer and mainframe systems.

3.3 Application of WATRAD to Seepage Area A

Total radium concentrations vary from approximately 10^{-13} to 10^{-15} molar in Seepage Area A. Although radium speciation by WATRAD is only suggestive, the resulting speciation calculations indicate that Ra^{2+} and $RaSO_4^0$ comprise > 99.9% of total radium. Consequently, it is reasonable to accept these two species as the likely dominant species based on WATRAD's calculations. Area A waters throughout the centerplane are significantly undersaturated with respect to all radium minerals in WATRAD and, thus, aqueous radium is probably not regulated by mineral solubility. Therefore, radium is likely regulated by co-precipitation or sorption of the 2 + cation (discussed in next section).

Total actinium concentrations are approximately $10^{-14} M$ and WATRAD suggests the dominant aqueous species are: $AcSO_4^+$ (about 80% of total Ac), Ac^{3+} (about 10%) and $Ac(SO_4)_2^-$ (about 10%). Within the accuracy of WATRAD calculations, these species may simply indicate that aqueous actinium exists primarily as cationic species in Area A. All actinium minerals in WATRAD are at extremely undersaturated levels in Area A and, thus, actinium is expected to behave as a cation, regulated by sorption and/or co-precipitation.

Total thorium concentrations are approximately $10^{-7} M$. Unlike radium and actinium, thorium speciation is sensitive to aqueous organic complexation, but the only organic species in WATRAD's thorium database are $EDTA^{4-}$ and oxalate $(C_2O_4^{2-})$. EDTA is an unusually strong complexer of thorium and is therefore probably unrepresentative of natural DOC (Dissolved Organic Carbon) complexing. By elimination, oxalate must be used to evaluate the sensitivity of Th-organic complexing in Area A waters. Table 3 shows that organic complexes are dominant if the reasonable assumption is made that the complexing capacity of the measured 5 ppm DOC can be approximated by that of 0.5–5.0 ppm oxalate as C. Table 3 also shows that M17 groundwater is significantly undersaturated with respect to crystalline $Th(OH)_4$ except if 5 ppm DOC is assumed to have the complexing capacity of < 0.05 ppm oxalate as C. The log SI value for $Th(OH)_4$ increases through the neutralization zone from an inner-core value of -10, suggesting $Th(OH)_4$ is not forming along most of the centerplane and its saturation index simply varies with pH. On the other hand, $Th(SO_4)_2$ is relatively near saturation at M17 and throughout much of the centerplane for reasonable assumptions on DOC complexing, suggesting $Th(SO_4)_2$ may regulate aqueous thorium. Despite the exact level of organic complexation, aqueous thorium is expected to exist primarily as an anionic complex (Table 3) and, consequently, the potential for sorption and co-precipitation is expected to be relatively minor along most of the centerline.

Total uranium concentrations vary from approximately 10^{-5} to $10^{-8} M$ along the centerplane of the plume. Organic complexes of uranium are predicted to represent a maximum of a few percent of total uranium in Area A and, thus, are considered minor. Uranium is a redox-active element that forms $4+$ (U^{4+}), $5+$ (UO_2^+) and $6+$ (UO_2^{2+}) species in solution and WATRAD indicates that total UO_2^{2+} comprises of 99.7% of total uranium, total UO_2^+ comprises 0.3% of total uranium, and total U^{4+} comprises about 10^{-7} of total uranium. For total UO_2^{2+},

TABLE 3

Effects of oxalate complexing on thorium speciation (piezometer M17 – 2.5 in 1980)

| Oxalate	Dominant species (and approx. % of total)		Log SI cryst. $Th(OH)_4$	Log SI $Th(SO_4)_2$
5 ppm C	$Th(C_2O_4)_4^{4-}$	(79%)	-5.55	-3.04
	$Th(C_2O_4)_3^{2-}$	(21%)		
0.5 ppm C	$Th(C_2O_4)_3^{2-}$	(70.0%)	-2.03	$+0.48$
	$Th(C_2O_4)_4^{4-}$	(26.2%)		
	$Th(C_2O_4)_2^{0}$	(2.4%)		
	$Th(SO_4)_2^{0}$	(1.0%)		
	$Th(SO_4)_3^{2-}$	(0.3%)		
0.05 ppm C	$Th(SO_4)_2^{0}$	(71.1%)	-0.21	$+2.31$
	$Th(SO_4)_3^{2-}$	(19.7%)		
	$Th(C_2O_4)_3^{2-}$	(4.7%)		
	$Th(C_2O_4)_2^{0}$	(1.6%)		
	$ThSO_4^{2+}$	(1.2%)		

the dominant aqueous species are $UO_2(SO_4)_2^{2-}$ (86.0% of total in the inner core at piezometer M1 to 51.3% at M17), $UO_2CO_3^0$ (1.9% at M1 to 36.7% at M17), and UO_2^{2+} (7.0% at M1 to 8.8% at M17). As a result, uranium may behave predominantly as a cationic, anionic, or neutral-charge complex along much of the plume centerline. For U^{4+}, the dominant species are: $U(OH)_3^+$, $U(OH)_4^0$, and $U(SO_4)_2^0$.

One 6+ and two 4+ uranium minerals are near saturation along most of the centerline from M1 to M17: $(UO_2)_2SiO_4$ (log SI generally $\pm$ 0.20 in 1982, but -3.0 in 1980), $USiO_4$ (log SI generally $\pm$ 1.5), and crystalline $U(OH)_4$ (log SI generally $\pm$ 0.90). Additionally, $Ca_2UO_2(CO_3)_2$, $CaMgUO_2(CO_3)_3$, and $Mg_2UO_2(CO_3)_3$ regularly approach saturation from undersaturation along the centerline and, within the outer zone, these uranium-carbonate minerals are generally near saturation or at supersaturation. Although all saturation indices are variable, they suggest that the precipitation of $(UO_2)_2SiO_4$, $USiO_4$, and $U(OH)_4$ may regulate uranium concentrations in the neutralization zone. The decrease of uranium by a factor of about 2500 (Table 2) over a relatively short distance also suggests that mineral precipitation rather than simple adsorption may be operating.

In summary, aqueous speciation of radium and actinium by WATRAD indicates that complexation modifies only to a minor degree their potential cationic sorptive behavior in Area A, and they are probably not affected by mineral precipitation. On the other hand, thorium exists in solution mainly as anionic complexes, and anions are not often significantly adsorbed at somewhat acidic pH. The speciation and resulting sorptive behavior of uranium is more ambiguous. Saturation indices suggest uranium and thorium may instead be regulated by mineral precipitation-dissolution.

4. SORPTION AND CO-PRECIPITATION CONTROLS

Adsorption as used in this paper refers to the removal of radionuclides from solution onto the aquifer matrix without any modification by precipitating minerals. In this study, adsorption is considered to be the simplification of ion exchange:

$$R\text{-aqueous} + M\text{-solid} \leftrightarrow R\text{-solid} + M\text{-aqueous} \qquad (2)$$
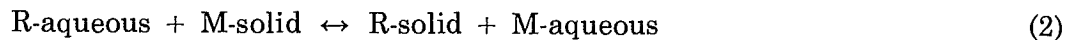
where R indicates a radionuclide and M is an initially adsorbed ion. In Area A, major ions such as ferrous iron probably represent M and, thus, aqueous concentrations of M are approximately 0.1 molar. On the other hand, R is 10^{-7} to 10^{-15} molar. As a result, the operation of eqn. 2 towards the right cannot be detected by a 10^{-7} to 10^{-15} molar increase in M-aqueous because of analytical precision. Additionally, such an undetectable increase in M-aqueous will not likely maintain a constant (equilibrium-based) ratio of products to reactants. As a result, the use of simple sorption for radionuclide partitioning by ignoring M in eqn. 2 is acceptable. The solid-liquid partitioning is examined here through a partitioning coefficient (PC), identical to a distribution coefficient (K_d) in measurement, but without any implication of reversibility and linearity.

Co-precipitation as used in this paper is the removal of radionuclides from solution under the influence of precipitation of one or more minerals ("carriers") in which radionuclides do not represent a major constituent. This definition does not, for example, differentiate between the incorporation of radionuclides into the carrier's crystal structure and the adsorption of radionuclides onto the carrier's surface during precipitation.

One simple method that can be used to distinguish the operation of adsorption from co-precipitation is the comparison of measured PC values in Seepage Area A against published K_d values of adsorption. A significant discrepancy of PC values from published data may imply the operation of co-precipitation. In order to calculate PC values for Area A, solid-phase concentrations are calculated, where measured data are unavailable, by the "cell-and-streamtube" approach developed in the first paper of this series (Morin et al., 1988). As a check on the reliability of this approach, a comparison of a calculated and a measured solid-phase radium concentration agrees at least within a factor of 4 (perhaps within a factor of 2 depending on the accuracy of the analytical methodology) and a similar check for uranium agrees within a factor of 1.5.

For total radium, PC values for the inner core, neutralization zone, and outer zone are 71, 6–20, and 167–360 mL g^{-1}, respectively. Published K_d values for total radium are naturally dependent on such factors as pH and soil type, but for conditions similar to Area A they range from 20 to 500 mL g^{-1} (Morin, 1983). Therefore, PC values suggest that adsorption of radium takes place in the inner core and outer zone, while the much lower PC value in the neutralization zone suggests that adsorption may be limited by mineral precipitation and that co-precipitation removes proportionally less aqueous radium than adsorption. Known carriers in the neutralization zone are siderite, based on the carrying ability of calcite, and gypsum.

Little is known on actinium sorption and co-precipitation, but there is a possibility that co-precipitation could dominate (e.g., Wahl and Bonner, 1951). The only known carriers of actinium found in Area A are Al-OH minerals and these minerals might then be regulating actinium. A PC value of about 100 mL g^{-1} is calculated from the "cell-and-streamtube" approach.

No solid-phase thorium concentrations were measured in Area A and the apparent trend of increasing aqueous concentrations with a decrease at M17 (Table 2) is not amenable to cell-and-streamtube calculations. Consequently, PC values are not available. Published K_d values for conditions similar to Seepage Area A are about 300 to 10,000 mL g^{-1} (Taylor, 1980) and adsorption would thus be expected to cause sharply decreasing concentrations along the centerline. As this decrease is not observed, adsorption is considered a negligible process. This is in agreement with the conclusion based on dominant anionic complexes of thorium in Area A. In addition, there are no known strong carriers of thorium forming in the neutralization zone, so co-precipitation is also considered negligible. Therefore, by elimination, precipitation-dissolution of Th(SO$_4$)$_2$ appears to be the main process regulating thorium concentrations.

Published K_d values for total uranium at neutral pH range from 1 to

$1000 \, mL \, g^{-1}$ apparently depending on aqueous complexation (Morin, 1983). Because uranium in Area A waters may predominantly occur as anionic complexes, a relatively low PC can be expected and the PC value in the neutralization zone is $37 \, mL \, g^{-1}$ based on measured concentrations. However, because this value lies in the K_d range, adsorption may be regulating total uranium concentrations. The only defined carrier of uranium known to be precipitating in the neutralization zone is $Al(OH)_3$ (Palei, 1970), but the carrying capacity of $Al(OH)_3$ is not defined. Consequently, the importance of co-precipitation remains undefined.

In summary, total radium concentrations in Seepage Area A are apparently regulated by sorption within the inner core and outer zone of the plume and possibly by co-precipitation with gypsum and siderite in the neutralization zone. Actinium is believed to be regulated by co-precipitation with Al-OH minerals. Thorium and uranium are likely regulated by mineral precipitation, although uranium adsorption and co-precipitation with Al-OH minerals cannot be ruled out.

5. ISOTOPIC ACTIVITY RATIOS OF MEMBERS OF THE NATURAL DECAY SERIES

As explained in the Introduction, the concentration of negligible-concentration isotopes of an element can vary by orders of magnitude and yet not invoke the geochemical process regulating the total concentration of the element and the dominant isotope. On the other hand, if the process is already operating, thereby decreasing or increasing the aqueous concentration of the dominant isotope, the concentrations of minor isotopes will be affected to some degree. In fact, the minor isotopes should display a behavior nearly identical to that of the dominant isotope because mass differences among the isotopes of Figs. 1–3 are often less than 2%. Through the neutralization zone of Area A, however, minor isotopes do not often behave exactly like the dominant isotope (Table 2), indicating parental behavior exerts an influence. For example, if the parent of a minor radium isotope is essentially all adsorbed, then essentially all of the radium isotope begins its life on the aquifer matrix. In order for this isotope to establish an aqueous concentration, it must oppose all of the adsorption, co-precipitation, and precipitation towards the solid phase occurring in the neutralization zone. As a further complication, if the parent's half-life is very short, then the parent will not engage in solid-liquid interactions and the grandparent's behavior becomes more important. Therefore, in order to completely define radionuclide behavior, the aqueous and solid-phase concentrations of all members of all decay series must be measured. This task is far beyond the scope of this study. Nevertheless, the effects of parental behavior, even if the parent is unmeasured, can sometimes be evaluated by the examination of various isotopic activity ratios within a decay series (Figs. 1–3).

For the ^{238}U series, the first ratio that can be examined in Area A is $^{234}U/^{238}U$ which increases from 1.23 to 3.92 (Table 4) through the neutralization zone. This indicates the water becomes relatively enriched in ^{234}U although activities

TABLE 4

Activity ratios for the natural decay series along the plume centerline

	M1	M20	M8	M16	M17	M19	
^{238}U series							
$^{234}U/^{238}U$	1.23	–	2.11	3.27	3.03	3.92	(1980)
$^{230}Th/^{234}U$	0.18	–	0.05	0.04	0.12	–	(1980)
$^{230}Th/^{238}U$	0.22	–	0.11	0.13	0.36	–	(1980)
$^{226}Ra/^{230}Th$	4.33	–	27.11	21.38	9.45	–	(1980)
	2.89	6.77	2.90	8.00	4.47	–	(1982)
$^{226}Ra/^{234}U$	0.78	–	1.22	0.91	1.14	0.20	(1980)
$^{210}Pb/^{226}Ra$	0.09	–	0.01	0.03	0.04	0.17	(1980)
	0.03	0.09	0.09	< 0.02	0.09	–	(81/82)
$^{210}Pb/^{238}U$	0.08	–	0.03	0.10	0.12	0.14	(1980)
^{235}U series							
$^{227}Th/^{227}Ac$	1.88	1.84	1.36	1.37	1.26	–	(1982)
$^{223}Ra/^{227}Th$	0.14	0.18	0.23	0.30	–	–	(1982)
$^{223}Ra/^{227}Ac$	0.26	0.33	0.31	0.41	0.37	–	(1982)
^{232}Th series							
$^{228}Th/^{232}Th$	0.62	–	0.66	> 4.89*	< 0.43	–	(1980)
	–	5.14	–	0.86	3.51	–	(1981)

*Value should be 0.23 based on calculated ^{232}Th from measured total thorium in Table 2.

of both isotopes decrease sharply. The only long-lived (on a geochemical scale) intermediate is ^{234}Th (half-life of about 24 days), which forms by alpha decay of ^{238}U. Therefore, a possible enrichment mechanism along the flowpath is a combination of alpha recoil of ^{234}Th off the aquifer matrix into solution and the more conservative aqueous behavior of total thorium until ^{234}Th decays to ^{234}Pa then quickly to ^{234}U. In any case, the aqueous behavior of ^{234}U is modified from that of total uranium and ^{238}U by parental behavior.

The $^{230}Th/^{234}U$ ratio (Table 4) displays relatively low values, which is expected where aqueous uranium exists predominantly in the 6+ state (Laul et al., 1985), and decreases within the neutralization zone then increases at M17. Because there are no intermediate radionuclides, this variation only reflects the differential behavior of these two species: ^{230}Th decreases sharply at the upgradient edge of the neutralization zone then remains relatively constant, while ^{234}U decreases gradually through the neutralization zone. The anomalous behavior of ^{230}Th relative to its parent and to total thorium cannot be easily explained, but could be the result of analytical problems (DeJong and Wiles, 1984).

The $^{226}Ra/^{230}Th$ ratio displays an inverse trend from that of $^{230}Th/^{234}U$. Because ^{230}Th is the direct parent of ^{226}Ra, this variation is again caused by the anomalous behavior of ^{230}Th relative to the gradual decrease in ^{226}Ra. It is interesting to note that, if ^{230}Th were not measured in Area A, the $^{226}Ra/^{234}U$ ratio (Table 4) would be used to evaluate ^{230}Th behavior. This ratio shows a

slight increase at the upgradient edge of the neutralization zone with a generally constant ratio through the neutralization zone and a possibly erroneous (based on M9 data in 1980 and M19 data in 1981) sharp decrease at M19. These relatively steady values for $^{226}Ra/^{234}U$ despite the variability in ratios using ^{230}Th indicate either the limitations of evaluating the behavior of intermediate radionuclides from ancester/descendant ratios or the analytical errors with ^{230}Th (DeJong and Wiles, 1984).

For the $^{210}Pb/^{226}Ra$ ratio in Table 4, the erratic ^{210}Pb values do not provide a clearly definable smooth trend. Little of the intermediate radionuclides such as ^{222}Rn gas is believed to be lost from solution because there is no regular decrease in the ratio along the centerline. The $^{210}Pb/^{238}U$ ratio, which spans most of the ^{238}U decay series, suggests that significant disequilibrium exists but does not appreciably change along the centerline.

For the ^{235}U decay series, there are no measured ^{235}U activities, although its descendants suggest its activity is high. The $^{227}Th/^{227}Ac$ ratio (Table 4) decreases from the inner core into the neutralization zone which may reflect the differing geochemical controls on thorium and actinium. The inverse trend is found for the $^{223}Ra/^{227}Th$ ratio. Like the ^{230}Th case, the granddaughter/grandparent ratio ($^{223}Ra/^{227}Ac$, Table 4) shows a discernible trend, but conceals the real or artificial trend in ^{227}Th.

For the ^{232}Th series, the only available ratio is $^{228}Th/^{232}Th$ (Table 4), which is at values of 0.62–0.66 to M8 then decreases in value through M17 in 1980. However, in 1981, values of the ratio are significantly higher and do not display a clear trend along the centerline.

In summary, evaluation of descendant-ancestor ratios indicates that the differential behavior of radium, actinium, thorium, and uranium can be seen in ratio changes along the flowpath. It is not clear from the data whether an intermediate radionuclide's aqueous behavior can be reliably inferred from the comparison of its ancestor/daughter behavior. Further exploration of this topic is limited without a great deal more aqueous and solid-phase measurements.

6. SUMMARY

The general geochemical behavior of radionuclides in uranium-tailings seepage is described and then applied to data from the field site, Seepage Area A of the Nordic Main impoundment. The behavior of a particular isotope of an element usually depends on the total elemental concentration as well as on the behavior of ancestor radionuclides of other elements. Radionuclide behavior is evaluated by: (1) calculation of total elemental concentrations from the isotopes; (2) calculation of complexation and mineral saturation indices by the program, WATRAD; (3) comparison of solid–liquid partitioning coefficients with published data to assess the importance of adsorption and co-precipitation; and (4) evaluation of the possible extent to which particular radionuclides

are influenced by ancestor behavior by using activity ratios of members within a decay series along a flowpath.

For Area A, total aqueous radium (essentially ^{226}Ra) probably occurs predominantly as the free cation and $RaSO_4^0$ and is apparently regulated by sorption within the inner core and outer zone and apparently by co-precipitation with gypsum and siderite within the neutralization zone. The behavior of ^{223}Ra is modified from that of ^{226}Ra by the geochemical behavior of the parent of ^{223}Ra, ^{227}Th. The general geochemical behavior of actinium is not well characterized in the literature; however, aqueous actinium likely occurs as cationic and anionic complexes and free Ac^{3+}. The co-precipitation of actinium with Al-OH minerals may regulate total actinium in the neutralization zone. Total aqueous thorium (essentially ^{232}Th) occurs as anionic complexes with sulfate and organic ligands. Total thorium concentrations may be regulated by the precipitation-dissolution of $Th(SO_4)_2$. Minor-concentration thorium isotopes display significantly different trends from that of total thorium and ^{232}Th as the result of parental controls. Total aqueous uranium (essentially ^{238}U) occurs predominantly in the 6+ state as anionic and neutral-charge complexes of sulfate and carbonate and as free UO_2^{2+}. Uranium concentrations are possibly regulated by precipitation-dissolution of one 6+ mineral, $(UO_2)_2SiO_4$, and/or two 4+ minerals, $USiO_4$ and crystalline $U(OH)_4$, within the neutralization zone. In the outer zone, uranium may be precipitating as $Ca-Mg-UO_2-CO_3$ minerals. Aqueous ^{234}U shows a relative 3-fold enrichment over ^{238}U along 21 m of flow path, indicating parental behavior significantly modifies ^{234}U behavior from that of ^{238}U.

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