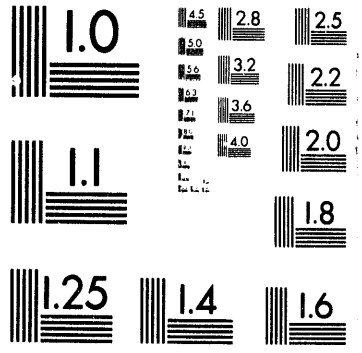
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U-234/U-238 RATIO: QUALITATIVE ESTIMATE OF GROUNDWATER FLOW IN ROCKY FLATS MONITORING WELLS

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DISCLAIMER

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ABSTRACT

The U-238 concentrations in Rocky Flats groundwaters vary from <0.2 to 69 pCi/l (1pCi = 3 ug). However, the activity U-234/U-238 ratios are low and range mostly 1.2 to 2.7. The low activity ratios can be interpreted to suggest that the groundwaters are moving slow (<1 meter/year); this is supported with an estimate of about a few ft/year based on hydrologic parameters [1]. Uranium is probably present in the +6 state, predominantly as a uranyl carbonate complexes UO_2CO_3 and $UO_2(CO_3)_2^{2-}$, because of the predominant bicarbonate medium.

INTRODUCTION

Groundwater movement through various pathways is the primary mechanism for the transport of radionuclides and trace elements in a water/rock interaction. About three dozen wells, installed in the Rocky Flats Plant (RFP) Solar Evaporation Ponds (SEP) area, are monitored quarterly to evaluate the extent of any lateral and downgradient migration of contaminants from the Solar Evaporation Ponds: 207-A; 207-B North, 207-B Center, and 207-B South; and 207-C. The Solar Ponds are the main source for the various contaminants: radionuclides (U-238, U-234, Pu-239, 240 and Am-241); anions; and trace metals to groundwaters.

The monitoring wells are shallow, 4 to 80 ft from the surface or 5836 to 5975 ft above sea level, and represent different segments of the two major geological hydrostrata units, Alluvium and Arapahoe bedrock, that underlie the Solar Evaporation Pond area. The bedrock consists of weathered clay stone and weathered and unweathered sandstone of the Arapahoe formation that underlies the Alluvium. The Alluvium consists of Rocky Flats Alluvium, Colluvium, and Valley Fill Alluvium that lie immediately beneath the Solar Ponds area. Based on the geology and stratigraphy, the Alluvium units are more permeable to groundwater than the Arapahoe bedrock units (US DOE, 1992) [1].

U-238 and U-234/U-238 ratios for 34 monitoring wells were evaluated for the first two quarters of 1992. The main objective was to evaluate if the disequilibrium of natural radionuclides in the U-238 chain, i.e., the ratio of U-234 to U-238, can be used to estimate groundwater flow qualitatively. Previous work by Laul and Smith (1988) [2] and Laul and Maiti (1990) [3] have shown that a qualitative estimate can be made from the U-234/U-238 ratio.

U-238 and U-234/U-238 Ratio

The disequilibrium of natural radionuclides in the U-238 chain can provide information on migration of radionuclides in groundwaters [2-6]. The U-234/U-238 ratios through a recoil mechanism can provide qualitative information as to whether the groundwater is moving slow or fast [2,3].

The U-234/U-238 ratios in groundwaters are typically observed at greater than unity (i.e. >1). The U-234 excess in groundwater (relative to its parent U-238) is the result of direct alpha recoil of U-238 to Th-234 followed by beta decay to U-234 (U-238 ^{alpha}--->Th-234 ^{beta}--->Pa-234 ^{beta}---> U-234) atoms across the solid/liquid boundary [2,4,7-11]. As a result of the alpha recoil process and beta decay of Th-234 to U-234, the U-234 becomes more mobile or leachable relative to U-238 in the solid due to the reduced bond strength as shown in Figure 1a. This isotopic fractionation mechanism results in the release of excess U-234 into the aqueous phase.

In a flowing system, the U-234/U-238 ratio is greater than unity in the aqueous phase and this ratio gradually increases with the increase in the groundwater flow. The U-234/U-238 ratios are 1.2 to 3.0 in slow or stagnant waters and 3 to 20 in moderate to fast moving waters, as shown in Figure 1b [2]. Sakanoue and Hayashi [12] and Sandoval et al. [13] reported high ratios (3 to 15) in Tatsunokuhi springs and Venezuelan hot springs. These high ratios can be interpreted due to a faster flowing system.

In a stagnant or closed system the U-234/U238 ratios are expected to approach unity, because the loss of U-234 that is preferentially transported by the water is replenished by the growth from the U-238 across the solid/liquid boundary, and the leached U-238 is not lost from the system. However, in reality the surface loss of U-234 can still result in ratios of 1.2 to 3.0 in stagnant or very slow moving waters. Ocean waters, a stagnant system, have a typical U-234/U-238 ratio of 1.15 [9].

Fig. 1a

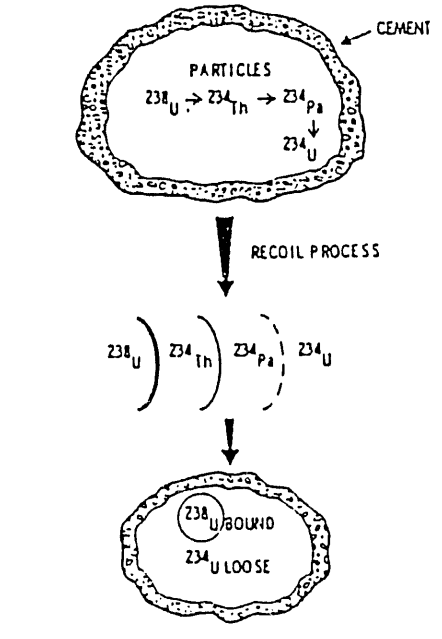

Fig. 1b

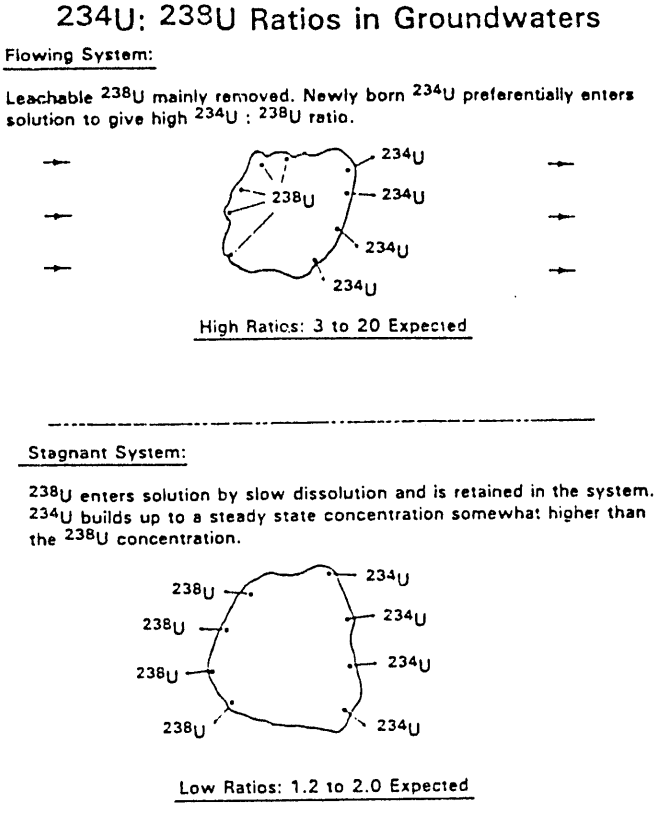

Figure 1a. A schematic diagram explaining why U-234 is more mobile than U-238.

Figure 1b. A leaching mechanism of U-234 relative to U-234 in flowing and stagnant systems (Laul and Smith 1988) [2].

DISCUSSION

In Rocky Flats groundwaters, the U-238 activity varies over two orders of magnitude and ranges from <0.2 to 69 pCi/l (1 ug of U-238 = 0.33 pCi), with a mean value of 13.6 pCi/l and a standard deviation of 17.9 pCi/l and the activity follows a log-normal distribution. Likewise, the U-234 activity ranges from <0.2 to 105 pCi/l with a mean value of 19.2 pCi/l and a standard deviation of 26.8 pCi/l, and the activity follows a log-normal distribution.

Many of the Arapahoe bedrock wells and a few of the Alluvium wells contain low uranium concentrations (<0.2 to 8 pCi/l), which probably represents background uranium levels. The U-234/U-238 activity ratios in these groundwaters range from 1.2 to 3.7, though the majority of the wells shows ratios between 1.2 to 2.7 (Figure 2). As discussed below, the low U-234/U-238 ratios can be interpreted to suggest that the groundwaters are moving slowly.

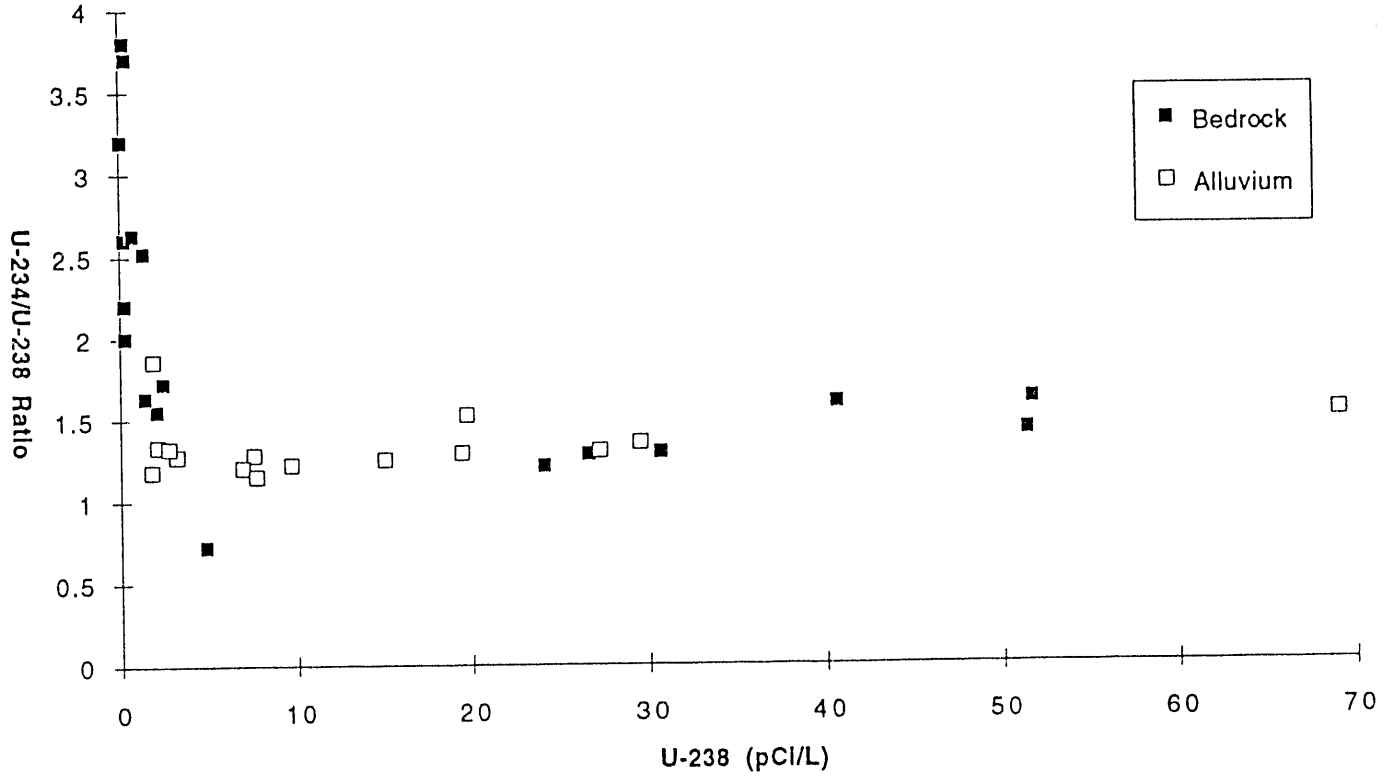

Figure 2. U-234/U-238 ratios versus U-238 (pCi/l) activity in Alluvium and Arapahoe bedrock monitoring wells. Most of the ratios lie between 1.2 to 2.7. Open square are Alluvium and closed squares are bedrock units.

Table 1. U-234/U-238 Ratio Versus Groundwater Flow

Well	Depth(ft)	U-234/U-238	Travel time	Comment
a. Palo Duro Brines				
Wolfcamp Brines				
Mansfield #1, Zone 1	4854	1.2	1 cm/yr	Th-He Age
Zone 2	4576	1.5	same	same
Sawyer #1, Zone 5	3180	1.5	same	same
Granitewash				
Sawyer #1, Zone 4	4300	2.4	1 m/yr	same
b. RFP, Groundwater	5840-5980			
	4-80 surface	1.2 to 2.7	<1 m/yr (assumed), slow flow	
			A few ft/year based on hydrologic parameters	
c. G.W (ORNL) Cm-244 (18 yr,5950 pCi/l)	shallow waste burial site			
--->Pu-240 (6580 yr)		8.3	2 m/yr, moderate flow	
d. J-13 Water, Yucca Mt. (NTS)	2430			
	943 surface	7.1	Moderate Flow (assumed)	
			A few meter/year based on hydrologic parameters	

Reference:

a. U-234/U-238 ratios are from Laul and Smith [2]; Th-He ages are from Delying et al [14].
b. Hydrologic parameters are from USDOE [1].
c. Marsch et al [15].
d. U-234/U-238 ratios are from Laul and Maiti [3]. Hydrologic parameters are from Czarnecki and Waddell [16] and SCP [17].

The U-234/U-238 ratios cannot be used to quantify flow rates; however, the ratios can provide a qualitative estimate. Table 1 summarizes the U-234/U-238 ratio versus groundwater flow for the various systems. Laul and Smith [2] observed low U-234/U-238 ratios for the Palo Duro brines, in which the travel time using Th--> He^4 aging was estimated at 1 cm/year for Wolfcamp brines and 1 meter/year for Granite Wash brines by Deyling et al. [14]. Using this range, one can place a limit of 1 meter or a few feet per year for the RFP groundwaters.

Using hydrologic parameters, Darcy velocity = (hydraulic conductivity) x (hydraulic gradient), and particle velocity (flow) = (Darcy velocity) / (bulk effective porosity). Hydraulic conductivity is estimated as 1.2×10^{-6} cm/sec [1], and hydraulic gradient can range from 0.01 to 0.1 and so is the bulk effective porosity. Assuming the bulk porosity of 0.1 and if the hydraulic gradient is 0.07, then the particle velocity is about 1 ft/year. There is a considerable uncertainty in the hydrologic parameters, however, a flow of few feet/ year appears reasonable, which is in agreement with a flow of <1 meter/yr based on the low U-234/U-238

ratios.

High U-238 contents (Figure 2) are generally associated with high nitrate (NO_3 +NO_2) contents and are used as an indicator of uranium contamination from the Solar Ponds. Thus, it could be argued that the observed U-234/U-238 ratios in the contaminated wells are dominated by the waste water leakage or seepage from the Solar Ponds, and thus have no relevance to the alpha recoil mechanism or slow moving groundwaters. The closer examination of the data reveal that the Pond waste water are not dominating the observed ratios in groundwaters. Further there are several wells in the Alluvium and Arapahoe bedrocks that contain virtually no nitrate (<1 mg/l), thus no contamination, and contain low uranium content and exhibit low U-234/U-238 ratios. Based on the uncontaminated monitoring wells, those low in uranium, the alpha recoil mechanism appears to be the dominant process in explaining the observed U-234/U-238 ratios in groundwater and consequently, implying slow moving groundwaters (<1 meter/year). This further implies that the contaminants are not moving very far in RFP groundwaters.

Marsh et al. (1993) [15] reported high Cm-244 activity (5950 pCi/l) in ground-waters near a shallow waste burial site at Oak Ridge National Laboratory. From the extent of contamination and the half-life of Cm-244 (18.1 yrs) and its daughter Pu-240 (6580 yrs), Marsh et al. [15] estimated a flow rate of 2 meters/year and observed a U-234/U-238 ratio of 8.3 for this groundwater, which suggests a moderately flowing system.

Laul and Maiti [3] observed a U-234/U-238 ratio of 7.1 in J-13 groundwater from the Yucca Mountain, Nevada test site (NTS), and suggested a moderately flowing system, consistent with the moderate hydraulic gradient from 3500 ft to 2000 ft in the Franklin Lake Playa area. Hydrologic parameters for the J-13 (Fortymile Wash area) tuffaceous rock in the Topopah Spring have been reported by Czarnecki and Waddell [16]. Hydraulic conductivity is estimated as 3.9 $x10^{-3}$ cm/sec and hydraulic gradient is 4.8 $x10^{-4}$. The porosity can range 0.001 - 0.1. Assuming bulk effective porosity of 0.1, the particle velocity is about 6 meter/year. There are somewhat different values quoted for the Topopah Spring in the Site Characterization Plan (SCP) [17]. Using these values of hydraulic conductivity - 1.1 $x10^{-5}$ cm/sec, hydraulic gradient - 1.1 $x10^{-4}$, and bulk effective porosity - 0.0028, the particle velocity is estimated as 14 meter/year [17]. There is a considerable uncertainty in the hydrologic parameters, however, a flow of few meter/year appears reasonable, which is in agreement with a moderate flow based on the U-234/U-238 ratio of 7.1.

Ludwig et al [18] reported large dispersion in the U-234/U-238 ratios (2.5 to 7) in various wells (J-12, J-13, JF3, Waterpipe Butte, Lathrop Wells and UE25P#1) from the Fortymile Wash, and they explained these ratios as a result of mixing of two-component members, which are not specified, and suggested other sources may be required. While mixing hypothesis can be a viable option, alternatively these ratios can be explained as the result of slow and moderate flow in Fortymile Wash.

Speciation of Uranium

Yucca Mountain contains vadose zones and uranium in J-13 groundwater, predominant in bicarbonate medium, contains uranium in the +6 state and probably as a uranyl bicarbonate complex.

Rocky Flats Plant contains vadose zones and shallow monitoring wells. This fact, coupled with the high nitrate (oxidizing agent) content, may tend to oxidize uranium (if any is in the +4 state) to the +6 state. Thus, uranium is most likely present in the +6 state in these groundwaters. The RFP groundwater compositions are predominantly sodium, magnesium and calcium bicarbonates. The bicarbonate ranges from 110 to 680 mg/l and the pHs of these wells are 7.5 +/- 0.5, which is consistent with the predominance of the bicarbonate medium, similar to J-13 water [3]. Based on this comparison, it seems that uranium in the RFP wells is present as uranyl carbonate complexes (UO_2CO_3 and $UO_2(CO_3)_2^{2-}$).

SUMMARY

- U-234/U-238 ratios seem to be applicable to provide a qualitative estimate of groundwater flow.
- U-238 concentrations in RFP groundwaters vary from <0.2 to 69 pCi/l; however, the U-234/U-238 ratios are low and range mostly 1.2-2.7. The low ratios can be interpreted to suggest that the groundwaters are moving slow (<1 meter/year), which is in agreement with an estimate of about a few ft/year (US DOE, 1991) [1].
- Uranium is probably present in the +6 state, predominantly as a uranyl carbonate complex, because of the predominant bicarbonate medium.

ACKNOWLEDGEMENTS

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