Assessing field-scale migration of radionuclides at the Nevada Test Site: "mobile" species

Q.H. Hu [a,b,*], T.P. Rose [c], M. Zavarin [c], D.K. Smith [c], J.E. Moran [c], P.H. Zhao [c]

[a] College of Water Sciences, Beijing Normal University, Xinjiekouwai Street 19, Beijing 100875, P.R. China
[b] Department of Earth and Environmental Sciences, University of Texas at Arlington, Arlington, TX 76019, United States
[c] Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550, United States

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ABSTRACT

Many long-lived radionuclides are present in groundwater at the Nevada Test Site (NTS) as a result of 828 underground nuclear weapons tests conducted between 1951 and 1992. In conjunction with a comprehensive geochemical review of radionuclides (^{3}H, ^{14}C, ^{36}Cl, ^{99}Tc and ^{129}I) that are presumably mobile in the subsurface, we synthesized a body of radionuclide activity data measured from groundwater samples collected at 18 monitoring wells, to qualitatively assess their migration at the NTS over distances of hundreds of meters and over timescales of decades. Tritium and ^{36}Cl showed little evidence of retardation, while the transport of ^{14}C may have been retarded by its isotopic exchange with carbonate minerals in the aquifer. Observed local reducing conditions (either natural or test-induced) will impact the mobility of certain redox-sensitive radionuclides (especially ^{99}Tc) that were otherwise soluble and readily transported under oxidizing conditions. Conversely, strongly oxidizing conditions may impact the mobility of ^{129}I which is mobile under reducing conditions. The effect of iodine speciation on its transport deserves further attention. Indication of delayed transport of some "mobile" radionuclides (especially ^{99}Tc) in the groundwater at the NTS suggested the importance of redox conditions of the natural system in controlling the fate and transport of radionuclides, which has implications in the enhanced performance of the potential Yucca Mountain repository, located adjacent to the NTS, to store high-level nuclear wastes as well as management of radionuclide contamination in legacy nuclear operations facilities.

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1. Introduction

At the Nevada Test Site (NTS), a large inventory of radionuclides (tritium, fission products, activation products, and actinides) is present in the subsurface environments as a result of 828 underground nuclear weapons tests (DOE/NV, 2000; Smith et al., 2003). Since 1973, various programs have been investigating the environmental effects of nuclear testing at the NTS. An appreciable body of information regarding radionuclide activity at the NTS groundwaters has been accumulated, and a synthesis of this information provides insight into field-scale radionuclide migration. Many of the radionuclides that are present in NTS groundwater from underground testing are also present in the high-level nuclear waste to be buried at the potential Yucca Mountain repository, which is located on the western edge of the NTS (Fig. 1). Among these radionuclides are ^{3}H (tritium), ^{14}C (carbon), ^{36}Cl (chlorine),

^{99}Tc (technetium), and ^{129}I (iodine) that presumably have large potential for migration, whereas the migration of sorptive ^{90}Sr (strontium), ^{137}Cs (cesium), ^{237}Np (neptunium), and uranium (U) and plutonium (Pu) isotopes may be retarded by sorption. Because of their comparable hydrogeologic settings, understanding gained from the NTS is directly applicable to the Total System Performance Assessment (TSPA) of the proposed Yucca Mountain repository.

Most nuclear tests at the NTS were conducted between ~500 and 1200 m below the land surface. Approximately 300 nuclear tests were detonated either below or within 100 m of the water table; the cavities produced by these tests have since refilled with water. Subsequent migration of radionuclides from the nuclear testing, observed in various monitoring wells, form the basis of this work. The geologic media that hosted the underground tests at the NTS consists primarily of tuffs, rhyolites, and tuffaceous alluvium. Similarly, Yucca Mountain consists of a group of north–south-trending block-faulted ridges composed of rhyolitic tuffs and lava flows. At approximately 12–13 km from the Mountain, the water table transitions from volcanic tuffs to alluvium (Eddebbarh et al., 2003).

The migration behavior of ^{99}Tc and ^{129}I is of particular interest in this study. Both nuclides are present in large abundance in underground test cavities and in spent reactor fuel. Because of their

* Corresponding author. College of Water Sciences, Beijing Normal University, Xinjiekouwai Street 19, Beijing 100875, P.R. China. Tel.: +1 817 272 2987; fax: +1 817 272 2628.
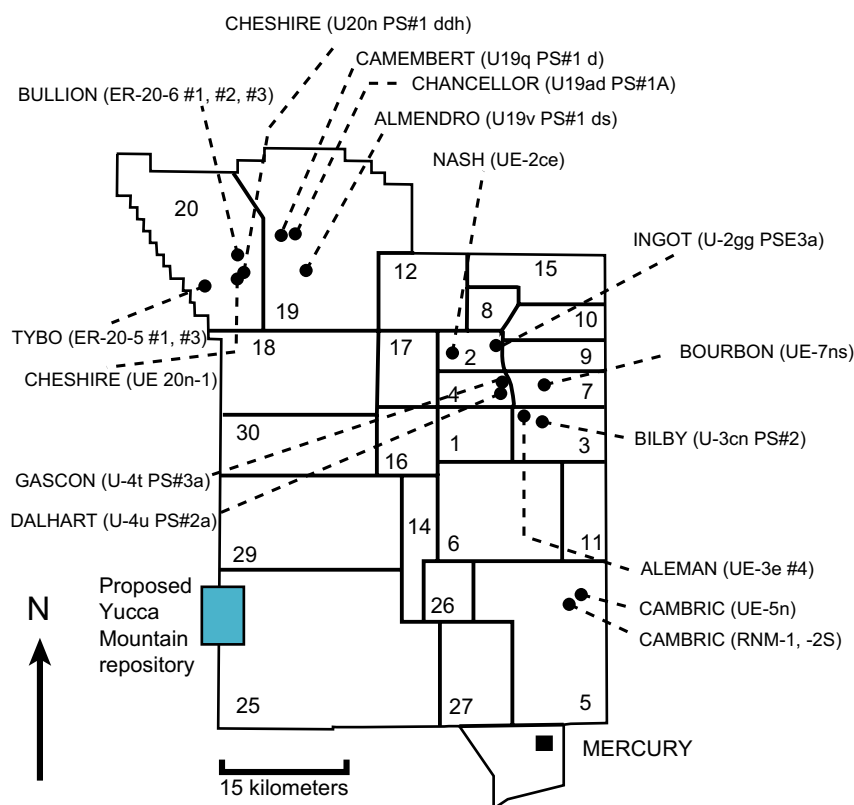E-mail address: huqinhong@yahoo.com (Q.H. Hu).

Fig. 1. Map of the Nevada Test Site (with an area about 3500 km²), and the potential Yucca Mountain repository, showing the near-field sampling sites. Both test name and associated near-field well (in parentheses) are provided. Numbers in subdivision are the area designations of the NTS.

long half-lives (2.13×10^5 and 1.57×10^7 years for ^{99}Tc and ^{129}I, respectively) and presumed mobile behavior in groundwater, both ^{99}Tc and ^{129}I are important dose contributors to the calculated health risk for many U.S. Department of Energy nuclear facilities, including the Nevada Test Site (Smith et al., 2003), Hanford Site (Kaplan and Serne, 1998; Um et al., 2004), Savannah River Site (Beals and Hayes, 1995), and Idaho National Laboratory (Beasley et al., 1998).

When studying radionuclide transport in the field, a distribution coefficient (K_d) approach has been commonly employed in transport codes to quantify the extent of radionuclide-water–solid interactions. The K_d data are commonly determined from laboratory batch and column experiments under oxidizing conditions. Values of K_d for a number of radionuclides were reported for representative geologic media, including alluvium, carbonate rock, and volcanic tuffs (devitrified, vitric, and zeolitic), encountered at the NTS (SNJV, 2005) and proposed Yucca Mountain repository (CRWMS M&O, 2000). Carbon and chlorine are considered to be nonsorbing (with K_d value of 0) in all representative tuffs encountered below the potential repository horizon. The K_d values of ^{99}Tc and ^{129}I in TSPA are 0 in all volcanic tuffs and 0.27–0.63 mL/g (weakly sorbing) in alluvium (CRWMS M&O, 2000). These values are based on the assumption that Tc and I exist as mobile anionic species [pertechnetate (TcO_4^-) and I^-] in Yucca Mountain groundwaters and during experimental measurements of K_d values.

However, both Tc and I are redox-sensitive radionuclides, and their speciation and retardation is sensitive to modest changes in redox conditions (e.g., Lieser and Bauscher, 1987; Arnold et al., 2006). By varying the redox potential, Lieser and Bauscher (1987) observed a change in the K_d value of about three orders of magnitude over a small range of Eh at 170 ± 60 mV and a pH of 7 ± 0.5. Potential variations in groundwater redox conditions along flow paths could result in much longer transport times than those predicted with minimal retardation. Valuable field-scale information to elucidate the natural controls on the mobility of these species

could be garnered from the groundwater monitoring program and migration experiments that have taken place at the NTS over the past 30 years.

By synthesizing available NTS data, a further understanding of the migration behavior of these "mobile" radionuclides at the NTS can be obtained in a cost-effective manner, at field scales over distances of hundreds of meters and under hydrogeologic conditions similar to the proposed Yucca Mountain repository. With a comprehensive review of the geochemical behavior of "mobile" radionuclides at the NTS, the objectives of this work are to (1) interpret available radionuclide activity data to qualitatively assess radionuclide migration in the subsurface of the NTS, (2) present evidence for changing redox conditions of the natural system and the resultant effects in controlling radionuclide speciation and migration, and (3) demonstrate enhanced retardation of ^{99}Tc from local reducing zones and discuss its implications for the performance of the Yucca Mountain repository. The paper begins with a discussion of radiologic vs. hydrologic source terms, continues with an analysis and review of NTS data for each radionuclide, discusses evidence for local reducing groundwaters at the NTS, and concludes by discussing the implications for radionuclide transport in subsurface systems (particularly for Yucca Mountain).

2. Radiologic and hydrologic source terms

The radiologic source term is the total inventory of residual radioactivity as a result of an underground nuclear test, while the hydrologic source term is the portion of radiologic source term that is available for groundwater transport. The partitioning of radionuclides among solid, liquid, and gaseous phases is a function of the physico-chemical properties (in particular, volatility) of the specific radionuclides, the nature of host geologic media, and the characteristics of test cavity formation and collapse.

Field investigations at the NTS and at French testing areas in the Pacific have yielded information regarding the initial distribution of radionuclides after a nuclear test (Smith, 1995; IAEA, 1998). The estimated partitioning of selected radionuclides among melt glass, rubble, water, and gas is shown in Table 1. The data in Table 1 originate from measurements derived from radiochemical diagnostics of nuclear tests (e.g., Borg et al., 1976), augmented by general thermodynamic properties (e.g., boiling points, vapor pressures) of these elements under extreme (high temperature and pressure) conditions. With the exception of ^{90}Sr and ^{137}Cs, the data apply to the general understanding of radionuclide distributions from underground nuclear testing. The partitioning behavior of ^{90}Sr and ^{137}Cs, with their short-lived gaseous precursors ^{90}Kr and ^{137}Xe, between rubble and melt glass is strongly dependent on the cooling history of the cavity as well as the presence of volatile, non-condensible gases (e.g., CO_2, H_2) in the cavity–chimney region.

In general, refractory elements (e.g., Pu, Am, Np, Ce, Eu) are largely incorporated into the melt glass that coalesces at the base of the cavity (Fig. 2). However, $\leq 5\%$ of the refractory material may be distributed more broadly in the cavity region if it is entrained with escaping cavity gases or as a result of splashing of the melt glass during cavity collapse (IAEA, 1998). More volatile species with low boiling points (e.g., tritium, Cl, I, Ru, U, Sb) tend to circulate up cracks in the rubble chimney that forms above the cavity. As the cooling progresses, the melt begins to quench, and species with lower boiling points subsequently condense onto exposed mineral and fracture surfaces within the cavity and the collapsed rubble. A portion of the volatile species can also be volumetrically incorporated into the melt glass. Tritium will condense as molecular HTO together with the large amounts of steam produced by the explosion. Fractions of volatile radionuclides with large solubilities (e.g., ^{36}Cl and ^{129}I) will also be partitioned into the condensed water in the cavity. Gas species (e.g., ^{90}Kr and ^{137}Xe), and consequently their daughter products ^{90}Sr and ^{137}Cs, could be transported through the rubble and distributed high up in the cavity–chimney region relative to the refractory radionuclides (Smith, 1998).

In tests conducted beneath the water table, groundwater from the periphery will invade the cavity–chimney and mix with the condensed water in the interstitial voids of the rubble and glass matrices. This will allow the "rubble", "water", as well as some of the "gas" fractions of the inventory to become incorporated in, and mobilized by, the groundwater, and for the "glass" fractions to be slowly leached (i.e., glass dissolution).

3. Groundwater samples

The NTS "hot" (near-field) wells refer to monitoring wells where the samples contain radionuclides above safe-drinking-water standards, defined on the basis of tritium. Some near-field wells were completed opportunistically in post-shot holes drilled into nuclear test cavities or chimneys for diagnosing device performance, and others were developed specifically for radionuclide transport studies. Because of cavity collapse and well plugging, fewer than 20 out of nearly 300 nuclear events in the saturated zone were available for sampling. The body of data accumulated over 30 years from these wells was used in this study to assess the distribution and mobility of radionuclides at the NTS.

It should be emphasized that each hot well is unique and represents a wide range of geologic and hydrologic conditions, radiologic source terms, and groundwater sample quality. Significant differences in sampling and analytical protocols have existed over the years, and caution should be exercised when comparing data from different wells. Samples that were collected using downhole submersible pumps are more likely to be representative of the bulk fluid composition in the near-field environment. However, several of the wells, particularly those that have been converted from post-shot holes, consist of a single 7-cm diameter carbon steel piezometer tube. In most cases, these wells have only been accessible using wireline bailers. Given that the fluid in the piezometer tube cannot freely circulate, samples collected from these sites tend to be of questionable quality than those produced from pumped wells. Sampling methods are noted in Table 2, along with other relevant information about 18 hot wells and associated nuclear tests. Dependent upon the sampling location, the monitoring wells are categorized as cavity–chimney or satellite wells in this work (Fig. 2).

A database was compiled containing radionuclide activity data from 18 monitoring wells for 14 nuclear tests at the NTS over the past 30 years, with a total of 1286 sampling events as summarized in Table 2. Analyses have been performed on both mobile (^{3}H, ^{14}C, ^{36}Cl, ^{99}Tc, and ^{129}I) and sorbing (^{90}Sr, ^{137}Cs, ^{237}Np, and uranium and plutonium isotopes) radionuclides that are relevant to the groundwater contamination at the NTS and performance assessment of the Yucca Mountain repository. However, this paper only presents the results for the "mobile" radionuclides.

4. Results and discussion

4.1. Tritium

Tritium (half-life [$t_{1/2}$] is 12.26 years) is the most abundant residual radionuclide from underground nuclear testing in terms of radioactivity. After the nuclear explosion, tritium is probably present in free-radical form, which is intimately mixed with and incorporated in the vaporized water at temperatures sufficiently high to cause dissociation of the water molecules (Crow, 1976). While noting that the chemical form of tritium is unknown at times shortly after an underground nuclear explosion, Tewes (1968) suspected that it probably exists as some type of hydride, such as silicon hydride, and later oxidized to tritiated water. Upon cooling, essentially all ($>98\%$) of the tritium occurs as tritiated water, with only a small proportion in the gas form (Stead, 1963; IAEA, 1998). Core measurements from the CAMBRIC test showed only 0.01–0.1% of the tritium activity was in the form of HT or CH_3T (Hoffman et al., 1977).

Excluding the RNM-1 well data, where tritium was pumped from the CAMBRIC test cavity during a 16-year forced-gradient experiment (Hoffman et al., 1977; Bryant, 1992; Tompson et al., 2002), the measured tritium activity in the cavity–chimney wells ranged from 2.9×10^5 to 1.1×10^7 Bq/L (Table 3). In comparison, the maximum permissible concentration (MPC) in US drinking water is 741 Bq/L. Most of the samples from the satellite wells also exceeded the MPC of tritium (see Table 4), with measured tritium activities ranging from 3.0×10^0 to 1.1×10^7 Bq/L.

Tritium is considered an ideal water tracer (Davis et al., 1980), although small amounts of tritium retardation have been reported in transport studies (e.g., van Genuchten and Wierenga, 1977; Gaber et al., 1995; Hu and Brusseau, 1996). In an aggregated tropical soil, Seyfried and Rao (1987) reported more tritium sorption from

Table 1
Estimated percentage distribution of radionuclides among the melt glass, rubble, gas, and groundwater following a typical underground nuclear test (IAEA, 1998); data in parentheses for ^{90}Sr and ^{137}Cs are from Tompson et al. (2002)

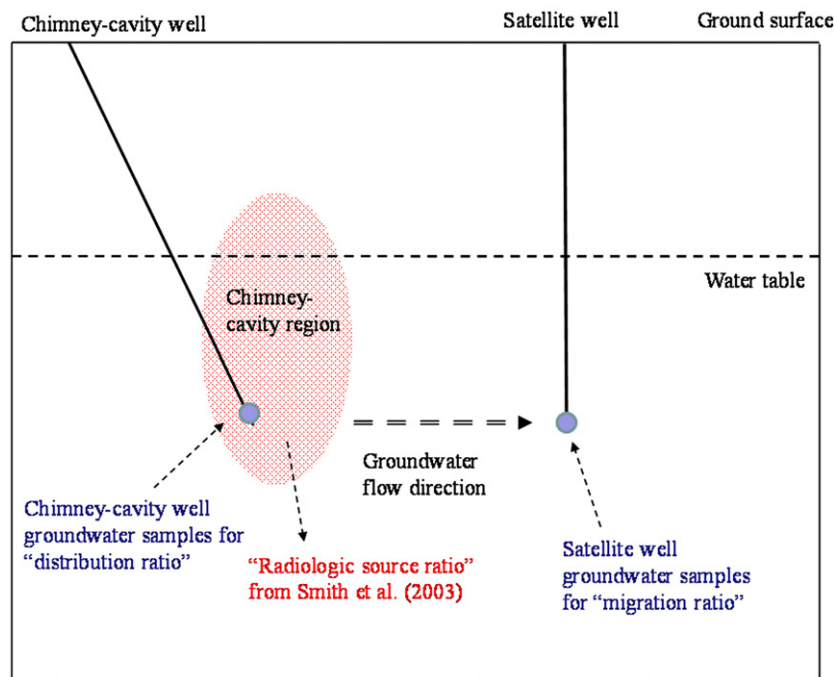| Radionuclide	Glass	Rubble	Gas	Water
^{3}H			2	98
^{14}C		10	80	10
^{36}Cl	50	40		10
^{90}Sr	40 (25)	60 (75)		
^{99}Tc	80	20		
^{129}I	50	40		10
^{137}Cs	25(10)	75(90)		
U isotopes	90	10		
^{237}Np	95	5		
Pu isotopes	98	2		

Fig. 2. Illustration of hypothetical cross-section for an underground nuclear test cavity–chimney and satellite sampling wells.

Table 2
Compilation of nuclear tests, hot wells, and sample collections

Test name	Test date	Working point below water table (m)[a]	Yield[b] (kilotons)	Rock type[c]	Sampling well	Sample collection method	Sampling location with respect to the test hole	Sample collection dates (total events)
ALEMAN	9/11/1986	28	<20	VTA	UE-3e #4	Pump/Pressure tube	58 m North	1993–1998 (2)
ALMENDRO	6/6/1973	360	200–1000	TCU	U-19v PS#1 ds	Bailer	Cavity–chimney region	1993–2006 (8)
BILBY	9/13/1963	206	249	WTA	U-3cn PS#2	Pump	Chimney region	1977–2004 (15)
				LCA	U-3cn #5		129 m Southeast	1980–1997 (3)
BOURBON	1/20/1967	-41	20–200	LCA	UE-7ns	Pump	137 m Southeast	1983–2005 (11)
BULLION	6/13/1990	53	20–150	TCU	ER-20-6 #1	Pump	166 m Southwest	1996–1998 (6)
					ER-20-6 #2		207 m Southwest	1996–1997 (4)
					ER-20-6 #3		296 m Southwest	1996–1998 (4)
CAMBRIC	5/14/1965	77	0.75	AA	RNM-1	Pump	Cavity	1974–2004 (25)
					RNM-2S		91 m from cavity	1975–1992 (950),[d] 1978–2003 (14)
CAMEMBERT	6/26/1975	646	200–1000	TCU	U-19q PS#1 d	Pump	Chimney region	1998–2003 (2)
CHANCELLOR	9/1/1983	−20	143	LFA	U-19ad PS#1A	Pump	Cavity	2004 (1)
CHESHIRE	2/14/1976	536	200–500	LFA	U-20 n PS#1 DDh	Pump	Cavity	1976–2005 (24)
					UE-20 n-1		~ 300 m from cavity	1987 (98),[e] 1988 (3)
DALHART	10/13/1988	163	<150	TCU	U-4u PS#2a	Bailer (before 1997); Pump (after 1997)	Chimney region	1992–2003 (6)
GASCON	11/14/1986	103	20–150	TCU	UE-4 t P#1	Pressure tube	~170 m to the South	1992 (2)
					U-4 t PS#3a		~54 m from cavity wall	1993 (1)
INGOT	3/9/1989	−63	20–150	VTA	U-2gg PSE3a	Bailer	65 m beneath cavity	1994 (2)
NASH	1/19/1967	−64	39	LCA	UE-2ce	Bailer	183 m from working point	1982–1984 (65),[f] 1978–2005 (26)
TYBO/BENHAM[g]	5/14/1975	135	200–1000	WTA	ER-20-5 #1	Pump	280 m Southwest	1996–2004 (5)
				LFA	ER-20-5 #3		280 m Southwest	1996–2004 (6)

[a] A negative number means that the working point is above the water table, but a test conducted within 100 m of the water table was defined as saturated because of the potential for downward migration of radionuclides from the test cavity.

[b] Announced yields are from DOE/NV (2000).

[c] VTA, vitric tuff aquifer; TCU, tuff confining unit; LCA, lower carbonate aquifer; AA, alluvium aquifer; LFA, lava flow aquifer; WTA, welded tuff aquifer.

[d] The Radionuclide Migration Experiment was conducted at CAMBRIC, with continuous pumping during 1975–1992. These nearly 1000 samples were analyzed for ^{3}H (mostly), as well as ^{36}Cl, ^{85}Kr, ^{99}Tc, and ^{129}I, with the results discussed in Hoffman et al. (1977), Burbey and Wheatcraft (1986), Ogard et al. (1988), Bryant (1992), Schroeder et al. (1993), Tompson et al. (2002), and Guell and Hunt (2003).

[e] Time-series samples at several sampling depths were collected from the pumping test at CHESHIRE site for the analyses of ^{3}H (mostly), as well as ^{36}Na, ^{85}Kr, ^{125}Sb, and ^{137}Cs; results were published and discussed in Buddemeier and Hunt (1988), Buddemeier et al. (1991), and Sawyer et al. (1999).

[f] Periodic samples were collected during 1982–1984 at the NASH pumping test for the analyses of ^{3}H, ^{90}Sr, and ^{137}Cs (Daniels and Thompson, 1984).

[g] The ER-20-5 well cluster was drilled in the near-field (~300 m from the surface ground zero) environment of the TYBO test. However, Pu isotopic signatures indicated the radionuclides in water samples from ER-20-5 wells are derived from the BENHAM test detonated ~1300 m up-gradient (Kersting et al., 1999).

Table 3
Compilation of "mobile" radionuclide activity from cavity–chimney wells at the NTS[a]

Test name	Sampling			Radionuclide activity (Bq/L)[b]					Normalized ratio[c]			
	Well	Depth (m)	Date	^{3}H	^{14}C	^{36}Cl	^{99}Tc	^{127}I	^{14}C/^{3}H	^{36}Cl/^{3}H	^{99}Tc/^{3}H	^{127}I/^{3}H
ALMENDRO	U-19v PS#1 ds	977	8/18/99	5.9E+6	1.3E+0	7.9E−2	2.8E−3	5.2E−2	1.2E−2	1.8E−3	4.2E−5	2.5E−1
		1006	9/26/00	5.6E+6	3.7E+0	1.4E−1	*4.0E−2*	1.0E−1	3.5E−2	2.3E−3	*6.1E−4*	5.0E−1
			5/31/01	6.7E+6	3.5E+0	1.3E−1	*4.0E−2*	8.6E−2	2.6E−2	1.5E−3	4.9E−4	3.4E−1
			7/23/03	5.2E+6	2.8E+0	2.1E−1	4.1E−4	9.4E−2	2.3E−2	4.3E−3	5.7E−6	4.2E−1
			4/18/06	4.1E+6		1.7E−1	3.7E−3			3.8E−3	5.5E−5	
		1091	9/22/98	5.9E+6	1.2E+2		7.4E−3		1.2E+0		1.2E−4	
BILBY	U-3cn PS#2	512–527	7/19/82	1.3E+6			1.5E+0				3.7E−1	
			6/18/85	1.0E+6			2.2E+0				5.6E−1	
			1/22/97	4.8E+5	6.4E+0	1.1E−2			4.1E−1	2.6E−3		
			12/18/01	3.7E+5	1.1E+1	1.6E+0	3.1E+0	5.8E−3	7.2E−1	3.7E−1	8.8E−1	5.8E−1
			12/9/04	2.9E+5	1.4E+1	9.4E−1	2.3E+0	9.3E−3	9.3E−1	2.3E−1	7.0E−1	9.8E−1
CAMBRIC	RNM-1	324–328	6/28/00	1.0E+1		1.6E−5	*4.0E−2*			1.4E−2	*7.4E+1*	
			6/3/04	1.3E+1	9.0E−2	1.6E−5	*1.3E−4*	2.2E−5	9.7E+0	1.3E−2	*7.7E−1*	3.5E+1
CAMEMBERT	U-19q PS#1 d	1402–1445	10/21/98	7.8E+5	4.8E+1	6.7E−4	3.1E−3	1.4E−4	3.6E+0	1.2E−4	8.6E−5	5.6E−3
			7/16/03	4.1E+5	1.1E+1	6.8E−4	4.0E−2	7.3E−5	1.2E+0	1.8E−4	3.8E−4	4.2E−3
CHANCELLOR	U-19q PS#1 d	795	9/27/04	8.1E+5	1.5E+1	3.4E−1	1.7E+0	7.2E−2	7.6E−1	4.2E−2	1.4E−1	1.9E+0
CHESHIRE	U-20 n PS#1 ddh	763–858 (*s*)	5/28/85	9.5E+6			1.8E+0				9.5E−2	
			11/7/85	8.6E+6				9.0E−3				1.6E−1
		838 (*s*)[d]	7/23/97	1.0E+6	1.4E+0				1.3E−1			
		812–913 (*s*)	7/28/98	1.4E+6	4.1E+0	9.1E−3	7.5E−1		2.6E−1	1.7E−3	1.2E−1	
		1206–1220 (*s*)	10/23/84	1.1E+7			1.9E+0	1.2E−2			8.5E−2	1.7E−1
			5/9/85	1.1E+7			1.9E+0				8.6E−2	
			9/21/98	2.4E+6	7.8E+0	1.5E−2	1.2E+0		2.9E−1	1.7E−3	1.1E−1	
			10/12/99	1.9E+6	7.4E+0	1.6E−2	8.2E−1	3.8E−3	3.3E−1	2.1E−3	9.6E−2	1.4E−1
			7/9/03	1.6E+6	6.8E+0	3.0E−2	4.6E−1	5.4E−3	2.8E−1	3.7E−3	5.0E−2	1.9E−1
			11/15/05	1.2E+6	6.6E+0	1.8E−2	3.4E−2	5.3E−3	3.2E−1	2.5E−3	4.4E−3	2.1E−1
DALHART	U-4u PS#2 a	472–501	9/23/98	6.0E+5			5.9E−1		4.2E+0		1.2E−1	
			8/16/99	5.9E+5	8.5E+0	3.2E−1	4.9E−1	1.1E−3	3.8E−1	5.2E−2	9.8E−2	7.5E−2
			10/9/03	9.8E+5	1.2E+1	1.1E+0	1.3E+0	4.9E−3	2.6E−1	8.5E−2	1.3E−1	1.6E−1
		512	7/21/97	5.8E+5	1.7E+0				9.1E−2			
		533	8/31/93	1.8E+6	*1.2E+2*				*2.4E+0*			

[a] Read 5.9E+5 as 5.9×10^5; values in italics are less than the specified detection limits.

[b] Radioactivity activity at the sample measurement. The maximum permissible activity in drinking water is 741, 119, 67, and 140 for ^{3}H, ^{14}C, ^{36}Cl, and ^{99}Tc (US Federal Register, 1991).

[c] Radioactivity for each radionuclide (RN) was first decay-corrected to September 23, 1992 (the date of the last underground nuclear test at the NTS), then divided by that of tritium; this ratio $(RN/^3H)_{GW}$ of each groundwater sample was finally divided by the $(RN/^3H)_{RS}$ ratio of average radiologic source term to derive the normalized ratio.

[d] (*s*) denotes the slanted distance between the borehole collar and sampling point.

batch adsorption experiments (K_d values of 0.13 ± 0.005 mL/g) than column transport studies (0.065 ± 0.004 mL/g). The interaction of tritium with solid surfaces has been postulated to occur via isotope exchange with clay lattice hydroxyl ions (Stewart and Baker, 1973) or water molecules in zeolite minerals (e.g., Andreev and Polevoi, 1996). The exchange is pronounced in kaolinite minerals that have available hydroxyl groups at platelet surfaces. In contrast, montmorillonite and illite minerals undergo exchange only at the edges of the plates (where the hydroxyl groups are available), and thus isotopic exchange is almost negligible (Gvirtzman and Margaritz, 1986). Stewart (1970) suggested that the interaction between tritium and solid surfaces depended upon moisture content and would be greater during the flow of tritiated water into initially dry soil than in saturated soils.

Appreciable sorption of tritium is not expected in most NTS tuffs because they do not contain a large amount of clays needed for tritium retardation. Some retardation may occur in zeolitized tuffs which contain large amounts of zeolite minerals (Rose et al., 2000a). Burbey and Wheatcraft (1986) reported that some tritium sorption was required to match the tritium elution curve at the CAMBRIC migration experiment located in high clay alluvium. However, Bryant (1992) cautioned that (1) the model fit with no tritium sorption was as good and (2) the magnitude of the reported K_d value (0.8 mL/g) by Burbey and Wheatcraft (1986) was unusually large. Nevertheless, Bryant (1992) speculated that although the retardation effect was relatively small, it might not be zero, which was consistent with previous studies discussed above.

4.2. Data analysis and uncertainty

Tritium is probably the best tracer for tracking radionuclide transport, and we used a ratio approach to assess the migration of other radionuclides (RN), with tritium as the reference nuclide (i.e., ^{99}Tc/^{3}H and ^{129}I/^{3}H). Depending upon the location of a monitoring well (cavity–chimney or satellite region), either a distribution or migration RN/^{3}H ratio was obtained (Fig. 2). All radionuclide activities have been decay-corrected to September 23, 1992, the date of the last underground nuclear test at the NTS. This allows us to directly compare the measured activity to a composite radionuclide source term reported in Smith et al. (2003). The composite radiologic source term sums the radionuclide inventories for individual tests in six principal geographic test centers. Test-specific, radiologic source term data, which are device-dependent (Pfingsten et al., 2001), are classified. The RN/^{3}H ratio for each groundwater sample was further divided by the "radiologic-source RN/^{3}H ratio" of the averaged source term inventory for the geographic test center wherein a particular nuclear test was located (from Smith et al., 2003) to obtain a "normalized ratio".

Data normalization provides us with an estimate of the relative radionuclide distribution and/or migration behavior, when compared to tritium. In other words, if a radionuclide behaves like tritium in its initial distribution following a nuclear test or during subsequent migration in the groundwater, the normalized ratio will be ~ 1. As a portion of the near-field wells sample the cavity–chimney region (Table 2), the normalized ratio will shed light on

Table 4
Compilation of "mobile" radionuclide activity from satellite wells at the NTS

Test name	Sampling			Radionuclide activity (Bq/L)					Ratio to tritium			
	Well	Depth (m)	Date	^3H	^{14}C	^{36}Cl	^{99}Tc	^{127}I	$^{14}C/^3H$	$^{36}Cl/^3H$	$^{99}Tc/^3H$	$^{127}I/^3H$
ALEMAN	UE3e4	658.4	9/23/98	2.4E+5			1.1E−3				5.7E−4	
BILBY	U-3cn #5	512–527	1/29/97	3.0E+0	4.2E−4	1.5E−5			4.4E+0	5.6E−1		
BOURBON	UE-7ns	617	8/21/01	1.7E+2	5.1E−3	5.2E−5	*4.0E−2*	2.2E−5	7.2E−1	2.6E−2	*3.8E+1*	4.9E+0
			12/13/05	3.6E+0	5.0E−3	9.0E−6	*1.6E−3*	1.5E−6	2.6E+1	1.7E−1	*2.5E+1*	1.2E+1
BULLION	ER-20-6 #1	743–898	12/17/96	9.4E+2	1.6E−2	1.2E−4			1.7E+0	3.8E−2		
			6/3/97	6.3E+2	7.5E−3	8.1E−5			1.1E+0	3.7E−2		
			8/27/97	1.2E+2	1.5E−3	2.0E−5			1.2E+0	4.8E−2		
			5/14/98	1.2E+2	1.5E−3	2.2E−5			1.2E+0	5.0E−2		
	ER-20-6 #2	743–898	11/27/96	6.3E+3	5.3E−2	6.4E−4			8.4E−1	3.0E−2		
			6/3/97	2.6E+3	2.7E−2	2.3E−4			9.9E−1	2.5E−2		
			7/17/97	2.6E+2	2.5E−3	2.5E−5			9.2E−1	2.8E−2		
	ER-20-6 #3	756–855	12/16/96	3.7E+1	7.9E−4	2.6E−7			2.1E+0	2.1E−3		
			6/2/97	3.7E+1	6.4E−4	7.7E−7			1.7E+0	6.0E−3		
			7/17/97	1.5E+2	9.1E−4	9.4E−6			5.9E−1	1.8E−2		
			5/13/98	4.1E+1	6.8E−4	1.2E−5			1.5E+0	8.0E−2		
CAMBRIC	RNM-2s	316–340	10/11/99	8.5E+3	3.1E−2	2.7E−3	3.6E−5	1.4E−5	6.4E−3	4.2E−3	4.2E−4	4.3E−2
			6/14/00	7.0E+3		2.9E−3	*4.0E−2*			5.3E−3	*5.5E−1*	
			5/9/03	5.6E+3	2.6E−2	4.3E−3	7.0E−3	3.3E−5	6.8E−3	8.2E−3	*1.0E−1*	1.3E−1
			7/10/03	4.8E+3	2.7E−2	3.8E−3	*1.3E−4*	5.0E−5	8.1E−3	8.4E−3	*2.1E−3*	2.2E−1
CHESHIRE	UE-20n-1	838	7/23/87	1.1E+7			1.7E+0	1.5E−2			6.4E−2	1.8E−1
GASCON	U-4tps#3a	322	8/31/93	2.5E+3	*1.2E+2*				*1.8E+3*			
INGOT	U-2gg PSE3a	587	9/22/94	2.4E+2	7.4E+2				1.1E+5			
		597	9/21/94	2.0E+2	2.2E+2				3.9E+4			
NASH	UE-2ce	427	8/22/01	5.2E+3	3.0E−2	3.1E−2	*1.3E−4*	1.2E−3	1.4E−1	5.1E−1	*2.6E−3*	8.3E+0
			7/12/05	3.5E+3	3.0E−2	1.7E−2	*8.9E−5*	8.9E−4	1.7E−1	3.3E−1	*2.2E−3*	7.6E+0
TYBO (BENHAM)	ER-20-5 #1	701–784	6/3/96	2.5E+6	2.3E+0	1.3E−1			9.7E−2	1.6E−2		
			4/22/97	1.9E+6	2.8E+0	1.1E−1			1.4E−1	1.6E−2		
			7/9/98	2.3E+6	6.6E+0	1.2E−1	1.0E−2	9.9E−3	2.6E−1	1.5E−2	1.0E−3	3.3E−1
			11/30/04	1.4E+6	8.3E+0	1.3E−1	1.3E−2	7.1E−3	3.8E−1	1.8E−2	1.6E−3	2.7E−1
	ER-20-5 #3	1046–1183	7/31/96	5.2E+3	7.0E−2	3.8E−4			1.4E+0	2.2E−2		
			4/22/97	4.0E+3	7.0E−2	3.5E−4			1.7E+0	2.6E−2		
			4/30/98	5.8E+3	6.4E−2	4.1E−4	*1.0E−3*		1.0E+0	1.9E−2	*1.5E+0*	
			11/15/01	5.2E+3	7.7E−2	8.1E−4	*4.0E−2*	4.4E−5	1.1E+0	3.5E−2	*1.7E+0*	5.4E−1
			10/29/04	1.4E+6	1.0E−1	1.3E−1	4.0E−2	5.2E−5	1.5E+0	2.2E−2	2.8E−2	6.6E−1

Values in italics are less than the specified detection limits.

the partitioning behavior (Section 2) in the aqueous, as opposed to the nonaqueous (melt glass and rubble) phase. A ratio significantly less than 1 suggests that a radionuclide (e.g., Pu) occurs predominantly in nonaqueous phases (Table 1). On the other hand, some monitoring wells are satellite wells located up to several hundred meters away from the cavity–chimney region, and in this case the normalized ratio helps elucidate the migration behavior of radionuclides; a ratio of ∼1 suggests the radionuclide migrates conservatively (like tritium) in groundwater.

To evaluate the uncertainty associated with using the geographic center-averaged radionuclide ratio to assess radionuclide migration, the radiologic source term $RN/^3H$ ratios for the CAMBRIC test were compared with the same ratios for the average inventory of the Frenchman Flat geographic center wherein CAMBRIC test occurred (Table 5). The CAMBRIC test is one of the few NTS events for which an unclassified radiologic source term estimate for some radionuclides is available (Hoffman et al., 1977; Schroeder et al., 1993). In this case, the test-specific and the average radionuclide source inventories differ by no more than a factor of 7. This suggests the normalized ratios have uncertainties that are within one order of magnitude. Also included in Table 5 are the radiologic source term $RN/^3H$ ratios for all the underground nuclear tests detonated at the NTS. For the majority of radionuclides, the difference between the $RN/^3H$ ratios for each geographic test center and the NTS total is within a factor of 3.

It should be noted that the CAMBRIC test had a relatively low yield of only 0.75 kt (DOE/NV, 2000). It is therefore of interest to

further assess how variations in the test yield may contribute to the uncertainty in $RN/^3H$ ratios. We analyzed the radiologic source term data for two nuclear test yields (5 and 100 kt) published in Pfingsten et al. (2001) for French underground tests (Table 6). The first row of data in Table 6 shows the activity ratio of each radionuclide for the two test yields (i.e., $^3H_{100}/^3H_5$). The second row of data shows the corresponding $RN/^3H$ ratios [i.e., $(RN/^3H)_{100}/(RN/^3H)_5$]. The normalized $RN/^3H$ ratio varies by no more than a factor of 8, with the ratio value being 2.9 and 1.8 for ^{99}Tc and ^{129}I, respectively (Table 6). This implies that uncertainties in the ratios resulting from variations in test yield are similar to the uncertainties associated with normalizing the data using geographic-centers averaged $RN/^3H$ ratios.

In general, we conclude that the comparison of $RN/^3H$ normalized ratios can provide a useful means of qualitatively assessing the field-scale migration behavior of mobile species in the complex subsurface of the NTS. If the classified test-specific radionuclide source term was used, the uncertainty would be reduced, but it is unlikely that it would change our conclusions.

4.3. Carbon-14

^{14}C ($t_{1/2}$ is 5730 years) occurs predominantly as dissolved bicarbonate ions in the NTS groundwater. Before 1996, ^{14}C was measured by liquid scintillation counting; more recently, it has been measured by accelerator mass spectrometry (AMS) with much better accuracy. Measured ^{14}C data were in the range of 0.09–118 Bq/L

Table 5
Comparison of activity RN/^{3}H ratios, decay-corrected to September 23, 1992, among CAMBRIC test, Frenchman Flat test center, and NTS total[a]

Location/Radionuclide	^{85}Kr	^{90}Sr	^{99}Tc	^{129}I	^{137}Cs	^{239}Pu	^{241}Am
CAMBRIC test	1.10E−04	1.74E−03	1.32E−06	5.13E−09	5.18E−03	1.50E−02	3.19E−03
Frenchman Flat test center	7.37E−04	1.08E−02	6.69E−06	2.60E−08	2.89E−02	8.11E−03	2.88E−03
NTS total	1.42E−03	1.73E−02	4.54E−06	1.40E−08	2.27E−02	1.27E−03	2.95E−04
Ratio between Frenchman Flat test center and CAMBRIC test	6.7	6.2	5.1	5.1	5.6	0.54	0.90

[a] Radiologic source term at the detonation date is from Hoffman et al. (1977) and Schroeder et al. (1993).

in the cavity–chimney wells, and were typically about two orders magnitude less in the satellite wells (Tables 3 and 4). The unusually high ^{14}C activities measured in the GASCON and INGOT satellite wells in 1993 and 1994 probably reflected large uncertainties in the analytical measurements.

Most normalized ^{14}C/^{3}H ratios at the cavity–chimney wells were close to 1 (Table 3), indicating that ^{14}C was present mostly in the aqueous phase in the cavity–chimney region. This is consistent with partitioning estimates in Table 1 that show ^{14}C is largely partitioned into the gas phase. Carbon-14 rapidly oxidizes to form CO_2, which is then readily dissolved as an aqueous species in groundwater. ALMENDRO samples consistently showed smaller ratios than other cavity–chimney wells. Groundwater in the ALMENDRO test cavity was postulated to be highly reducing, resulting in the breakdown of dissolved inorganic carbon to form methane gas. Evidence for reducing conditions is further discussed in Section 4.7. For the DALHART and BOURBON tests, the ^{14}C data exhibited variations of more than one order of magnitude among samples collected at different times (Tables 3 and 4). These variations may reflect sample collection bias in the stagnant borehole fluid. The first sample at the DALHART well was collected in 1997 using a wireline bailer whereas the later three samples were pumped, though only a small (<27 m^3) amount of fluid was purged prior to sampling. BOURBON samples were also bailed in 2001 and 2005.

The normalized ratios for ^{14}C/^{3}H at most satellite wells were generally similar to those at cavity–chimney wells. This suggested that the mobility of dissolved ^{14}C is similar to that of tritium in saturated volcanic-hosted aquifers. However, the only pair of cavity-satellite wells with available ^{14}C/^{3}H data was from the CAMBRIC test, which showed three orders of magnitude difference between the cavity (RNM-1) and satellite well (RNM-2s) well 91 m away. Tompson et al. (2002) also reported that the ^{14}C ratio from the far-field monitoring well (UE-5 n) is 10 times lower than its discharge source (RNM-2s) at the CAMBRIC vadose zone test. In this case, the retarded transport of ^{14}C was most likely related to isotopic exchange with carbonate-bearing minerals in the alluvial aquifer material.

4.4. Chlorine-36

^{36}Cl ($t_{1/2}$ is 3.01×10^5 years) occurs as the chloride anion in groundwater. For the NTS groundwater samples, the atom ratio of ^{36}Cl/Cl was measured by AMS, and the concentration of ^{36}Cl was calculated using the stable chloride concentration from ion chromatography. The surface charge for many clay minerals is predominantly negative, repelling the negative charge carried by anions. As a result, chloride is not expected to sorb onto geologic media. It has been postulated that "anion exclusion" may result in a greater average velocity for anions (such as chloride) relative to neutral water molecules. For a soil that contained 40% clay, Thomas and Swoboda (1970) found that the rate of chloride movement was 1.37 times faster than that of deuterium. During the CAMBRIC pumping experiment at the NTS, the breakthrough and the maximum concentration of ^{36}Cl appeared slightly ahead of tritium in alluvium (Ogard et al., 1988). This was attributed to the anion exclusion effect, which was inferred to inhibit ^{36}Cl$^-$ from entering the intragranular porosity of the soil matrix. The calculated anion exclusion volume of the alluvium at the NTS was 7.0 mL of liquid per 100 g of soil (Ogard et al., 1988). Both anion exclusion and anion sorption have been reported in various geologic media (e.g., McMahon and Thomas, 1974; Chan et al., 1980; Gvirtzman et al., 1986; Ishiguro et al., 1992; Seaman, 1998; Katou et al., 2001; Hu et al., 2005). The process and magnitude of these effects are dependent upon the clay mineralogy, clay content, saturation state, iron oxide content, and anion concentrations (Thomas and Swoboda, 1970; Applet et al., 1975; James and Rubin, 1986). Without complete information of these parameters, it is difficult to ascertain whether anion exclusion or anion sorption is operative.

Apart from the ^{36}Cl data of the CAMBRIC forced-gradient migration experiment discussed in Ogard et al. (1988), we present the ^{36}Cl data at other monitoring wells at the NTS. Measured ^{36}Cl activities at NTS monitoring wells varied by five orders of magnitude in both cavity–chimney and satellite wells, and the normalized ^{36}Cl/^{3}H ratios varied by up to three orders of magnitude (Tables 3 and 4). Some of the variation in the normalized ratios may reflect large uncertainties (up to a factor of 10) in the radiologic source term estimated for activation products (e.g., ^{36}Cl) (Smith et al., 2003). Qualitatively, the satellite wells had normalized ^{36}Cl/^{3}H ratios that were similar to the cavity–chimney wells, as observed at the BILBY and CAMBRIC sites, where paired samples from both types of wells were available. However, the distribution ratios (i.e., ^{36}Cl/^{3}H ratio for the cavity–chimney wells) were consistently much less than 1, which may indicate difference in the physico-chemical partitioning behavior of ^{36}Cl and ^{3}H immediately following an underground nuclear test. This was consistent with the IAEA (1998) partitioning estimate, wherein 50% of the ^{36}Cl was inferred to be present in melt glass (Table 1). The release of radionuclides from the melt glass is dependent on the slow process of glass dissolution, and ^{36}Cl in the glass is effectively unavailable for transport over short timescales.

4.5. Technetium-99

^{99}Tc is a long-lived ($t_{1/2} = 2.13 \times 10^5$ years), high-abundance (6% yield) fission product. NTS hot-well water samples were first analyzed for ^{99}Tc by radiochemical counting (Silva et al., 1988). A small number of NTS samples were later analyzed for ^{99}Tc by AMS, which provides much greater sensitivity and precision than conventional radiochemical counting (Bergquist et al., 2000). Recently, we have developed a routine and robust method to concentrate, purify, and

Table 6
Comparison of inventory for various radionuclides among two test yields (processed data from Table 3 of Pfingsten et al., 2001)

Radionuclide (RN)	^{3}H	^{14}C	^{36}Cl	^{55}Fe	^{60}Co	^{90}Sr	^{99}Tc	^{106}Ru	^{129}I	^{137}Cs	^{147}Pm
RN$_{100 \text{ kt}}$/RN$_{5 \text{ kt}}$[a]	6.31	1.25	28.1	19.7	20.5	47.3	18.4	3.97	11.3	17.1	21.8
(RN/^{3}H)$_{100}$/(RN/^{3}H)$_5$	1	0.20	4.5	3.1	3.2	7.5	2.9	0.63	1.8	2.7	3.5

[a] A ratio of radionuclide source term (in Bq) for test yield of 100 kt to 5 kt.

use a quadrupole ICP-MS to analyze ^{99}Tc in NTS groundwaters (Zhao et al., 2008).

Depending upon the redox conditions, Tc exists in two stable oxidation states. It forms a reduced species [predominantly Tc(IV)] at redox potential (Eh) values below about 220 mV with respect to standard hydrogen electrode (SHE) in neutral pH conditions. At higher Eh, it occurs as Tc(VII)O$_4^-$. Due to its weak interaction with mineral surfaces, TcO$_4^-$ is considered as one of the most mobile radionuclides in the environment. In contrast, transport of Tc(IV) species (TcO$_2 \cdot n$H$_2$O) are expected to be strongly retarded because of sorption and/or precipitation . Tc(IV) species become associated with solid phases through either hydrolysis or formation of strong surface complexes with Al and Fe oxides and clays (Burke et al., 2005) The solubility of TcO$_2 \cdot n$H$_2$O(s) in carbonate-containing groundwater was reported to be about 10^{-8} M (Eriksen et al., 1992). Similarly, chemical equilibrium modeling of groundwater at Yucca Mountain indicated a maximum Tc solubility of 4×10^{-9} M under reducing condition (Arnold et al., 2006). Experiments conducted on sediment-groundwater samples in Germany showed dramatically different sorption coefficients for Tc among aerobic and anaerobic conditions (Lieser and Bauscher, 1987). By varying the redox potential, they observed a change in the K_d value of about three orders of magnitude over a small range of Eh at 170 ± 60 mV and a pH of 7 ± 0.5.

The presence of reductants in the aquifer matrix (e.g., Fe(II) and S^{2-} as in pyrite) can contribute to the reduction of Tc(VII) to Tc(IV). Fe(II) minerals in igneous rocks can reduce TcO$_4^-$ and lead to sorption on mineral surfaces (Bondietti and Francis, 1979). Under reducing conditions, Cui and Eriksen (1996b, 1998) reported that TcO$_4^-$ was reduced to sparingly soluble TcO$_2 \cdot n$H$_2$O(s) by the Fe(II)-containing fracture-filling material and that Tc(IV)$_{aq}$ was rapidly sorbed by the material. Reduction of Tc(VII) to Tc(IV) occurs with Fe(II)-containing solid phases but not by aqueous Fe(II) species (Cui and Eriksen, 1996a). During the CHESHIRE migration experiment, ^{99}Tc activity was observed to decrease significantly for groundwater samples with high iron content, while ^{36}Cl was not affected (Buddemeier et al., 1991). The reduction of Tc(VII) to Tc(IV) and the formation of insoluble precipitates are the most likely mechanisms for the reduced mobility of ^{99}Tc.

During the CAMBRIC pumping experiment, Schroeder et al. (1993) reported that ^{99}Tc appeared to migrate a bit more slowly than ^{36}Cl. The initial breakthrough for ^{99}Tc was similar to tritium, but the migration rate of ^{99}Tc, evaluated from the center of mass, appeared to slightly exceed that of ^{3}H, perhaps as a result of anion exclusion effects. However, the data evaluation was based on a very limited number (one in RNM-1, and three in RNM-2s) of ^{99}Tc measurements. A ^{99}Tc/^{3}H ratio of 2.8×10^{-7}, decay-corrected to the CAMBRIC detonation date (May 14, 1965), was reported for the CAMBRIC source term and an activity ratio of 3.4×10^{-11} was measured in the cavity water (Schroeder et al., 1993). This indicated that only 0.01% of the ^{99}Tc source term was in the aqueous phase and available for transport.

Fig. 3a presents the measured concentration for ^{99}Tc and ^{3}H decay-corrected to September 23, 1992. Tritium concentrations in the cavity–chimney wells ranged from 9.8×10^{-10} (DALHART) to 3.0×10^{-8} M (ALMENDRO), corresponding to a radioactivity of 1.0×10^6–3.2×10^7 Bq/L. The concentration of ^{99}Tc varied from 6.7×10^{-15} (ALMENDRO) to 4.9×10^{-11} M (BILBY), which was much less than the solubility limit, with corresponding activities of 4.1×10^{-4}–3.1 Bq/L. While the activity plot in Fig. 3a shows the extent of radionuclide contamination in the groundwater from underground nuclear tests, it does not provide a straightforward way to evaluate the migration behavior, which is the focus of this work.

Fig. 3b shows a plot of test-specific ^{99}Tc/^{3}H ratios in groundwater normalized to the ^{99}Tc/^{3}H ratios of the radiologic source term for the geologic testing area in which each test occurred. The

normalized ^{99}Tc/^{3}H ratios in the BILBY, CHANCELLOR, CHESHIRE, and DALHART cavity–chimney wells were mostly in the range of 0.1–1. This indicated that as little as 10% of ^{99}Tc (compared to 98% for ^{3}H) produced from nuclear tests was present in the aqueous phase of cavity–chimney region. This value was close to the estimated partitioning of ^{99}Tc by the IAEA (1998), which suggested that 20% exists in the relatively accessible rubble phase (Table 1). The possibility that a large proportion (80%) of Tc could be incorporated into the melt glass is due to the fact that the fission chain precursors of ^{99}Tc includes ^{99}Zr ($t_{1/2} = 2.2$ s), ^{99}Nb ($t_{1/2} = 15.0$ s), and ^{99}Mo ($t_{1/2} = 2.75$ days), all of which have low or moderate volatilization in the underground testing environment. Fig. 3b shows that the normalized ^{99}Tc/^{3}H ratios in the groundwater from the ALMENDRO and CAMEMBERT tests were much lower than other cavity–chimney wells, which probably reflected a reducing chemical environment at these sites (to be discussed in Section 4.7).

Ratios of ^{99}Tc/^{3}H observed for wells RNM-1 and RNM-2s during the CAMBRIC pumping experiment were consistent with the presence of oxygenated water at CAMBRIC site (Bryant, 1992), wherein ^{99}Tc exists as mobile TcO$_4^-$ species. ^{99}Tc may also occur predominantly as TcO$_4^-$ at the CHESHIRE test, where uniform ^{99}Tc/^{3}H ratios were observed in the cavity, tuff formation, and satellite measurements (Buddemeier et al., 1991); cavity–chimney and satellite well data from CHESHIRE showed consistent normalized ^{99}Tc/^{3}H ratios near 0.1 (Fig. 3b). Recent measurements on samples from the CHESHIRE cavity exhibited a decreasing trend for ^{99}Tc/^{3}H ratios, indicating that the hydrologic source term in the cavity had been significantly diluted by the in-filling groundwater; the dilution effect was more significant for ^{3}H than ^{99}Tc because a major portion of ^{99}Tc source term was bound in the solid test debris.

The ^{99}Tc/^{3}H ratios at three other satellite wells (ALEMAN, NASH, and TYBO/BENHAM) were about two orders of magnitude lower than the cavity–chimney ratios at CHESHIRE and other sites with oxidizing groundwater (Fig. 3b). Although cavity–chimney wells were not available at these sites, one possible interpretation of these data was that field-scale migration of ^{99}Tc could be slower than that of tritium, with an apparent retardation factor as large as 100.[1] Delayed transport of ^{99}Tc may occur if locally reducing conditions are encountered along groundwater flow paths at the NTS, as discussed in Section 4.7. Under these circumstances, the Yucca Mountain TSPA recommendation for a K_d value of zero in tuff for ^{99}Tc may be too conservative, and natural redox barriers in the NTS subsurface could yield performance in retarding ^{99}Tc transport to downgradient receptors.

4.6. Iodine-129

As with ^{99}Tc, ^{129}I is a long half-lived fission product ($t_{1/2} = 1.57 \times 10^7$ years) with a unique and complex chemistry in the environment. Iodine-129 was routinely analyzed as ^{129}I/^{127}I ratios on an AMS. The fate and transport of ^{129}I in groundwater is dictated by its chemical speciation. Aqueous iodine usually occurs as the highly mobile iodide anion (I$^-$). Under more oxidizing conditions, iodine may be present as the iodate anion (IO$_3^-$), which is more reactive than iodide and could be sorbed onto positively charged sites locally existing in clays and organic matter (Couture and Seitz, 1983; Sheppard and Thibault, 1992). In contrast to ^{99}Tc, iodine has a minimal retardation under reducing conditions when iodide is the predominant form, and multiple iodine species (iodide, iodate,

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[1] Using the relationship between R_f and K_d ($R_f = 1 + (K_d \rho_b / \theta)$), with ρ_b the bulk density (g/cm^3), θ the volumetric water content (cm^3/cm^3), and typical ρ_b (1.87) and θ (0.236) values for NTS rock samples from Flint (2003), a K_d value of 12 mL/g is obtained for the R_f value of 100.
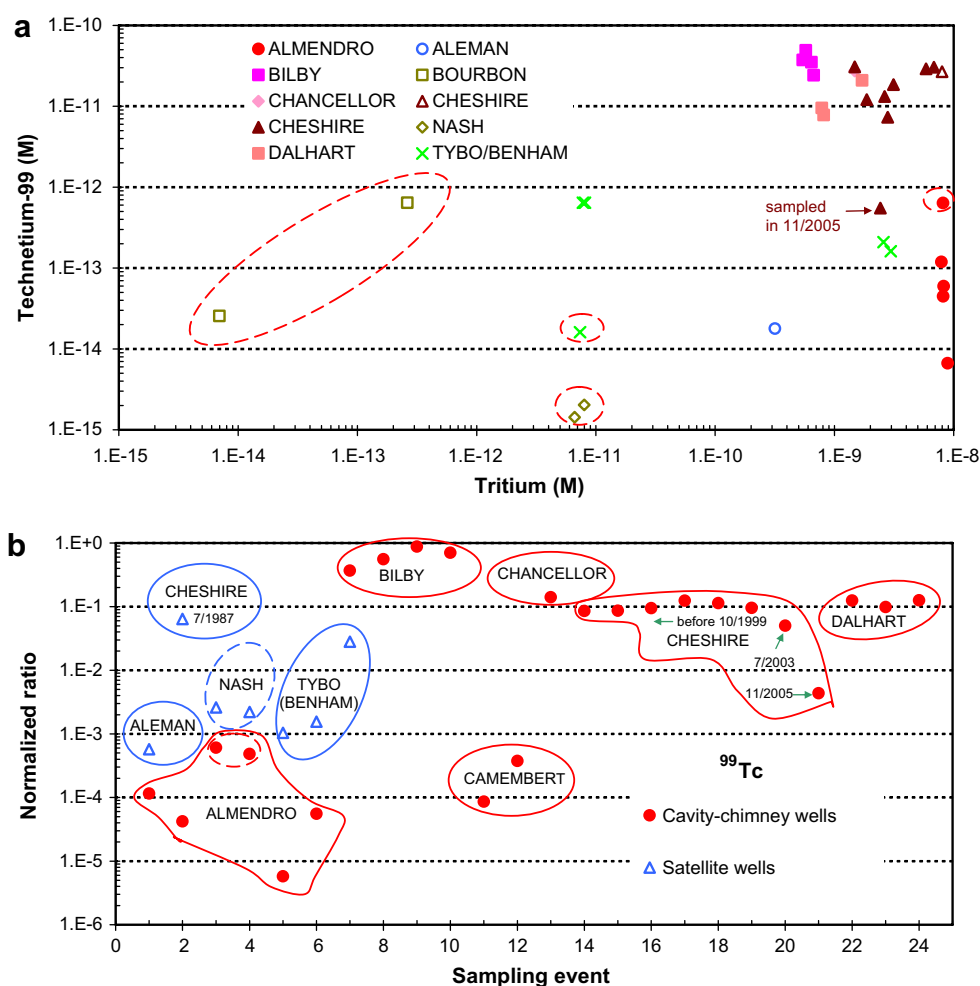
Fig. 3. (a). Plot of ^{99}Tc vs. tritium concentration (M), decay-corrected to September 23, 1992, for NTS near-field groundwater samples. Filled symbols are for cavity–chimney wells, and open ones for satellite wells. Dashed circles indicate that ^{99}Tc data are less than the detection limit. (b). Normalized activity ratios for ^{99}Tc/^{3}H. Samples with ^{99}Tc values less than the detection limit, which could vary depending upon the measurement approach and sample volume used, are shown as dashed circles. CAMBRIC data (a total of six) are not presented as five values are below the detection limit and could be misleading; the CAMBRIC migration experiment has indicated that ^{99}Tc migrates slightly faster than ^{3}H at oxidizing CAMBRIC groundwater (Schroeder et al., 1993). Also not shown are BOURBON data (2), which are all less than the detection limit. For a well with multiple sampling events, the data are shown with the latest sampling event at the most right-hand side.

and organic iodine species) are known to coexist in various aqueous systems (cf., Hu et al., 2005).

Fig. 4a presents the measured concentration for ^{129}I and ^{3}H decay-corrected to September 23, 1992. Excluding the CAMBRIC site wherein forced-gradient pumping test was conducted, tritium concentrations in the cavity–chimney wells ranged from 5.4×10^{-10} (BILBY) to 1.0×10^{-8} M (ALMENDRO), corresponding to a radioactivity of 5.8×10^{5}–1.1×10^{7} Bq/L. The concentration of ^{129}I varied from 9.4×10^{-14} (CAMEMBERT) to 1.3×10^{-10} M (ALMENDRO), with corresponding activities of 7.3×10^{-5} to 0.1 Bq/L. Furthermore, the concentration of ^{129}I in satellite wells varied from 1.9×10^{-15} (BOURBON) to 1.9×10^{-11} M (CHESHIRE), with corresponding activities of 1.5×10^{-6}–0.015 Bq/L.

During the CAMBRIC pumping experiment, a substantial fraction of the ^{129}I in the RNM-1 cavity well migrated to the RNM-2s satellite well, and a much smaller fraction of the ^{129}I was either immobile or is retarded to some extent (Bryant, 1992). It was postulated that reactive HIO was the predominant species that may interact with matrix materials. This work also confirmed that ^{129}I migrated at a slower rate than ^{3}H. We have observed lower ^{129}I/^{3}H ratios in RNM-2s than in RNM-1, though the results from RNM-2s have varied over time (Table 4; Fig. 4b) perhaps because of the complex speciation and geochemical behavior of iodine species.

The ^{129}I/^{3}H ratio at RNM-1 was unusually large (35), which was likely related to additional ^{129}I being released from the melt glass and rubble into the groundwater after the 17-year pumping experiment, while tritium activity in the groundwater had already been depleted.

CHESHIRE is another test in which both cavity and satellite well samples are available. Nearly identical ^{129}I/^{3}H ratios were observed at both CHESHIRE wells during a pumping experiment in the 1980s. Although the CHESHIRE satellite well was no longer sampled, the ^{129}I/^{3}H ratio in the cavity–chimney well has remained fairly constant over two decades of sampling. Additional pairs of cavity and satellite well samples were not available, though it was notable that both types of wells generally showed an overlapping range in ^{129}I/^{3}H ratios (Fig. 4b). The normalized ^{129}I/^{3}H ratio value was abnormally large (nearly 10) for the BOURBON and NASH tests. These samples were from carbonate aquifers and were either sampled by bailing or after pumping a limited volume. The enrichment in ^{129}I/^{3}H ratios could be related to the different geochemistry of the carbonate aquifer groundwater, and in particular, the presence of organic carbon derived from the chemical weathering of carbonate rocks or shales (Di-Giovanni et al., 2003). Dissolved organic carbon in groundwater is known to form strong complex with iodine. Overall, the available data show that it is likely that iodine species
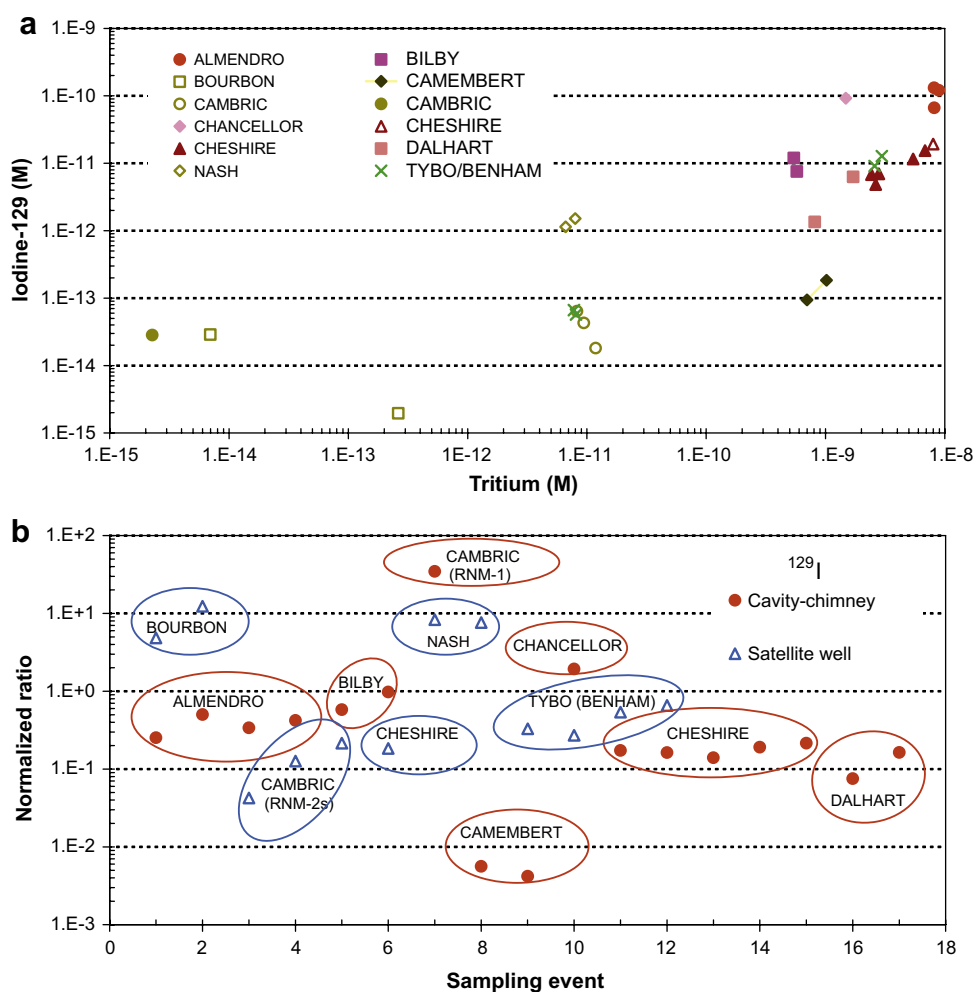
Fig. 4. (a) Plot of [129]I vs. tritium concentration (*M*), decay-corrected to September 23, 1992, for NTS near-field groundwater samples. (b) Normalized activity ratios for [129]I/[3]H.

are migrating conservatively with tritium at the NTS, which is not surprising as mobile iodide is the major iodine species under normal oxidizing conditions in the saturated zone.

Locally strongly oxidizing conditions may increase the presence of high-valence-state iodine species that are more reactive with geological media. In a leachate of a tuff sample collected from an underground nuclear explosion in hole U7ajs, Wolfsberg (1978) reported the existence of at least three iodine species: IO_4^-, IO_3^-, and I^-, with proportions of 10, 40, and 50%, respectively. This leachate was further used for batch sorption–desorption studies using alluvium samples from the CAMBRIC site, and a very large distribution coefficient value of 640 ± 300 mL/g was obtained. Strongly oxidizing conditions are most likely to occur in underground test cavities that lie above the water table, where atmospheric oxygen is present. Interaction with infiltrating groundwaters will occur only sporadically. This situation is somewhat analogous to the conditions that will exist at the proposed Yucca Mountain repository above the water table.

4.7. Redox chemistry of cavity and NTS groundwater

To understand the non-conservative transport of ^{99}Tc and [129]I, it is important to consider the redox chemistry of both the cavity water and local groundwater at the NTS, as summarized below. The study of Borg (1975) found direct evidence for a reducing cavity environment during the first few minutes after a nuclear detonation, when the melt glass was formed. Chemical analyses of melt glass samples from the RAINIER test in 1957 and PILEDRIVER test in 1966 showed the conversion of ferric iron (Fe^{3+}) to ferrous (Fe^{2+}) ion, which indicated that a reducing atmosphere prevailed in the cavities at the time of quenching. This was, in part, because of large quantities of metallic iron placed near the underground nuclear device, including engineering materials and diagnostic cables (Bryant and Fabryka-Martin, 1991).

Whether the test cavity water remains reducing depends upon its hydraulic connection to the groundwater. While test cavities such as CAMBRIC and CHESHIRE appeared to be hydraulically well connected to the surrounding flow system, our studies of the ALMENDRO and CAMEMBERT test cavities indicated a poor hydraulic connection at these sites. If groundwater circulation was sufficiently restricted, reducing conditions may persist for decades. For example, anomalously enriched $\delta^{13}C$ values in ALMENDRO groundwater samples suggested that methanogenesis was occurring (Rose et al., 2000b). Likewise, analysis of a gas sample from the CAMEMBERT post-shot hole showed that a significant depletion in oxygen ($0.12 \pm 0.01\%$) and enrichment in hydrogen gas ($8.28 \pm 0.01\%$) and methane (1%). This is characteristic of the anoxic, reducing condition favorable to methanogenesis. For methanogenesis to occur, the redox potential is expected to be less than -244 mV/SHE (at pH 7), which would indicate a strongly reducing environment at these tests.

We used a Dionex Corp. (Sunnyvale, CA) ion chromatography DX-600 system to measure low (sub-ppb) concentrations of iodide in NTS groundwater samples (Hu et al., 2005). The pulsed

amperometric detector had a detection limit of 0.6 µg/L for iodide. Total iodine was analyzed by ICP-MS with a detection limit about 0.1 µg/L. Total iodine is expected to be composed of both inorganic (i.e., iodide, iodate) and organic iodine species. Currently there are no low-detection methods to independently measure all of the potential inorganic and organic iodine species. The approach used here provides information about the proportion of total iodine existing as iodide, which is an indication of redox condition. Nine samples from the CAMBRIC site wells showed less than 10% of iodine species existing as the iodide anion, consistent with the strongly oxygenated groundwater at CAMBRIC site. In contrast, iodide comprised more than 60% of total iodine in ALMENDRO and CAMEMBERT wells which have been independently confirmed to be reducing. Among a total of 43 NTS groundwater samples (34 from near-field wells) that were analyzed for iodide and total iodine, 79% of the samples had iodide concentrations of less than 50% of the total iodine. This indicates that a considerable amount of ^{129}I may exist as potentially non-conservative species. The implications of changing redox state, as indicated from iodine speciation, are compartively less significant for iodine than for Tc, because of the large difference in the solubility and migration potential of Tc between $+7$ and $+4$ valence states.

Below the water table, where gas exchange with the atmosphere diminishes, dissolved oxygen (DO) may be gradually consumed by microbial activity, biodegradation of organic matter, and oxidation of reduced mineral phases in the aquifer. Under these conditions, deep aquifers (>250 m) may be moderately reducing because they are isolated from the atmosphere. Although the water table at the NTS ranges from 400 to 700 m deep below the ground surface, the groundwater has been generally assumed to be oxygenated (Winograd and Robertson, 1982; Coles and Ramspott, 1982; Buddemeier and Hunt, 1988).

Recent *in situ* redox measurements in NTS boreholes suggest that the groundwater is not uniformly oxidizing, and may have locally reducing zones. Since 2000, Finnegan et al. (2005) have employed a Hydrolab Minisonde 4a multi-probe to measure the *in situ* oxidation–reduction potential (ORP) and dissolved oxygen (DO) in non-radionuclide-contaminated wells at the NTS. From a total of 22 wells, a wide range of ORP and DO values were observed. The measured redox potential indicates that water was oxidizing (redox potential ranges from about 200 to 400 mV) in seven wells, mildly reducing (about -100 to 200 mV) in seven wells, and reducing (from -300 to -100 mV) in eight wells. Note that the measured redox potentials were not corrected to Eh/SHE values (add about 200 mV to the redox potential to convert to Eh), yet either potential can serve as a relative indicator of redox conditions of the groundwater. Overall, the ORP values corresponded with the DO values, and decreased with the increasing depth of measurement below the water table. The occurrence of reducing groundwater at the NTS seems to be geographically randomly distributed, yet is possibly related to the host lithology (e.g., presence of pyrite FeS_2) of these sampling wells. However, there are some concerns about whether measurements in non-purged wells are representative of the ambient conditions of the NTS groundwater. Measurements of stagnant water could be compromised by the potential corrosion of steel casing in some well bores.

Meijer and coworkers examined variations in the redox potential in groundwaters pumped from 20 boreholes in the saturated zone along potential transport pathways from Yucca Mountain (BSC, 2004; Arnold et al., 2006). At least three borehole volumes of groundwater were purged prior to sampling. Redox conditions in the water were characterized by the measurement of various parameters including ORP/Eh, DO, and the concentrations of redox-sensitive constituents such as ferrous iron, total iron, total manganese, nitrate, nitrite, ammonium, sulfide, sulfate, antimony, arsenic, and selenium. The boreholes in which reducing groundwater were observed included those on or near Yucca Mountain, a borehole in alluvium to the east of Fortymile Wash, and a group of boreholes to the west of Fortymile Wash near Yucca Mountain. The boreholes on Yucca Mountain that contained reducing waters were relatively deep ($\sim$ 900 m below the water table) boreholes that penetrated the Tram Member of the Crater Flat Tuff. This member included a volcanic unit that contains pyrite, which was a likely source of the reducing conditions. It is important to recognize that the presence of reducing conditions in more than one borehole located directly to the east of the repository footprint suggests there may be a volume of rock in this area that contains reducing groundwater. This volume ("reducing barrier") could provide an effective natural barrier to the transport of redox-sensitive radionuclides in the saturated zone. Boreholes to the east and west of Fortymile Wash near the southern boundary of the site were also known to contain pyrite based on core descriptions (BSC, 2004).

There is ongoing work to determine, using a coupled HPLC/ICP-MS method, the redox properties of groundwater near Yucca Mountain and at the NTS based on speciation of trace metals including As, Sb, Se, Cr, Mn, Cu, Mo, V, W, and U (Cizdziel et al., 2007). There appeared to be pockets of groundwater with locally reducing conditions, and in some cases greater percentages of reduced species as a function of depth within the same well.

Variations in redox conditions have also been documented in other deep aquifer systems. For example, variations in the concentrations of dissolved Fe species, H_2S, DO, and Eh were used to identify changes in redox conditions along a flow in the Carrizo Sand aquifer of Texas (with a sampling distance of 66 km and well depth ranging 122–1420 m from the recharge to discharge area) and the Upper Floridan carbonate aquifer of Florida (a sampling distance of 144 km and well depth 61–155 m) (Haque and Johannesson, 2006a,b). In both aquifers, oxic to suboxic conditions were observed near the recharge area, while mildly reducing groundwaters existed further down the flow path.

4.8. Implications of changing redox conditions on transport of redox-sensitive radionuclides

Radionuclide-water–solid interactions, such as the enhanced retardation of ^{99}Tc from localized reducing zones encountered along groundwater flow paths, could significantly contribute to the delayed transport of otherwise mobile radionuclides. Transport simulations in the unsaturated zone below the potential repository at Yucca Mountain showed that 10% of released nonsorbing ^{99}Tc ($K_d = 0$ mL/g) will travel through the unsaturated zone to reach the water table ($\sim$300 m below the repository horizon) in 300 years and 50% will reach the water table in 4000 years (Moridis et al., 2000). After arriving in the saturated zone, the transport times for nonsorbing radionuclides (such as ^{129}I and ^{99}Tc) were on the order of hundreds of years to reach the compliance boundary located 18 km from the potential repository (Arnold et al., 2003; Eddebbarh et al., 2003). Even modest amounts of radionuclide sorption onto the rock matrix can significantly reduce these transport rates. For example, 10% and 50% of released radionuclide with moderate sorption, with K_d values 1 mL/g for devitrified and vitric tuff and 4 mL/g for zeolitized tuff, will travel through the unsaturated zone for as long as 10,000 and 120,000 years, respectively (Moridis et al., 2000). Such delayed transport of radionuclides and improved performance of a proposed repository are also expected for redox-sensitive radionuclides when a reducing zone is encountered in the saturated zone.

Numerical simulations showed the enhanced sorption within a reducing zone of modest width, and associated larger K_d values, leaded to considerable retardation of redox-sensitive radionuclides (^{99}Tc) in the saturated zone (Arnold et al., 2006). The understanding of field-scale behavior of radionuclides, such as ^{99}Tc, obtained from

the NTS data can be used to examine their transport behavior, and reduce the conservatism in input parameters adopted in the TSPA analyses for Yucca Mountain repository. As a simple example, consider the difference in ^{99}Tc activity in the oxidizing groundwater at the CHESHIRE site when compared with the reducing groundwater at ALMENDRO. Both sites are located in the same geographic testing center, but the average normalized ^{99}Tc/^{3}H ratio at CHESHIRE was 8.1×10^{-2} ($n = 8$) while that of AMLENDRO was 2.2×10^{-4} ($n = 6$) (data from Table 3). In terms of measured activities, the average tritium activity at CHESHIRE and ALMENDRO was 5.0×10^6 and 5.6×10^6 Bq/L, respectively, whereas the average ^{99}Tc was 1.1 and 1.6×10^{-2} Bq/L, respectively. Despite similarities in the geologic setting (volcanic rock) and average tritium activity at CHESHIRE and ALMENDRO, the different redox conditions in these test cavities have resulted in groundwater ^{99}Tc activities that differed by approximately two orders of magnitude.

Localized reducing regions in the vadose zone can also affect radionuclide transport. For example, Zachara et al. (2004) and He et al. (2004) showed that local reducing conditions occurred in the Hanford vadose zone where caustic dissolution of iron-bearing phases, such as chlorite, biotite, magnetite, ilmenite, has released Fe(II) into solution. Based on a long-term (11 years) Pu mobility test in the unsaturated zone at Savannah River Site, Kaplan et al. (2004) reported that Pu was cycled through the $+4$ and $+5$ oxidation states as the redox status of the system changed in response to wetting and drying cycles, and not considering such natural oxidation processes could underestimate the Pu mobility. Overall, the potential impact on radionuclide transport from episodic flow under natural conditions (e.g., rainfall, fluctuating groundwater table) has been little studied, and is one of the most important coupled processes that still lacks sufficient understanding to be factored into remediation strategies at the contaminated sites.

5. Conclusions

In this study we synthesized a body of radionuclide activity data accumulated over the past several decades at the NTS. The results provided an independent qualitative evaluation of the field-scale transport of "mobile" radionuclide at field scales over distances up to 300 m. In general, ^{14}C, ^{36}Cl, and ^{129}I tended to be transported conservatively with tritium in groundwater. Migration of ^{14}C can be retarded by isotopic exchange on carbonate minerals in the aquifer. ^{36}Cl transport may appear to be slightly enhanced compared to tritium because of anion exclusion, combined with a slight delay of tritium transport resulting from its isotopic exchange with clay or zeolite minerals.

Knowledge of the speciation and reactions of multi-valent radionuclides, such as ^{99}Tc and ^{129}I, is very important for understanding their transport behavior at the NTS and Yucca Mountain and for managing and remediating radionuclide contamination at legacy nuclear operations facilities. Technetium occurs as the mobile and conservative species TcO_4^- under oxidizing conditions, but is relatively immobile as Tc(IV) under moderately reducing conditions. The speciation and migration behavior of ^{99}Tc is controlled by the redox conditions within the nuclear test cavity (initial distribution) and the surrounding groundwater flow system (subsequent migration). The chemical environment of a nuclear test cavity is inferred to have a reduced nature immediately following a detonation; reducing conditions may persist for decades in underground test cavities if the system remains isolated from the surrounding groundwater flow system. Furthermore, recent geochemical measurements at wells across the NTS and close to Yucca Mountain indicated that groundwaters are not uniformly oxidizing, as previously believed. Natural redox barriers associated with zones of reduction (e.g., pyrite-bearing horizons) within an aquifer would tend to inhibit the mobility of radionuclides in the

groundwater from the underground nuclear tests or breached nuclear fuel waste package to contribute to the enhanced performance of a potential geological repository at Yucca Mountain. The speciation and migration behavior of ^{129}I is also dependent upon redox conditions, but in this case the transport behavior may be most strongly inhibited when highly oxidized species are present, such as IO_3^-. Laboratory experiments, performed under varying controlled redox states, are currently underway to evaluate the transport of redox-sensitive radionuclides (especially Tc, Np, and I) with representative geological media and groundwater at the NTS.

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