



LAWRENCE  
LIVERMORE  
NATIONAL  
LABORATORY

# Neptunium Transport Behavior in the Vicinity of Underground Nuclear Tests at the Nevada Test Site

P. Zhao, R. M. Tinnacher, M. Zavarin, R. W. Williams, A. B. Kersting

January 3, 2011

## **Disclaimer**

---

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

# Neptunium Transport Behavior in the Vicinity of Underground Nuclear Tests at the Nevada National Security Site

P. Zhao, R. M. Tinnacher, M. Zavarin, R. W. William, A. B. Kersting  
Chemical Sciences Division, Lawrence Livermore National Laboratory

## Abstract

We used short lived  $^{239}\text{Np}$  as a yield tracer and state of the art magnetic sector ICP-MS to measure ultra low levels of  $^{237}\text{Np}$  in a number of “hot wells” at the Nevada National Security Site (NNSS), formerly known as the Nevada Test Site (NTS). The results indicate that  $^{237}\text{Np}$  concentrations at the Almendro, Cambric, Dalhart, Cheshire and Chancellor sites, are in the range of  $3 \times 10^{-5}$  to  $7 \times 10^{-2}$  pCi/L and well below the MCL for alpha emitting radionuclides (15 pCi/L) (EPA, 2009). Thus, while Np transport is believed to occur at the NNSS, activities are expected to be well below the regulatory limits for alpha-emitting radionuclides. We also compared  $^{237}\text{Np}$  concentration data to other radionuclides, including tritium,  $^{14}\text{C}$ ,  $^{36}\text{Cl}$ ,  $^{99}\text{Tc}$ ,  $^{129}\text{I}$ , and plutonium, to evaluate the relative  $^{237}\text{Np}$  transport behavior. Based on isotope ratios relative to published unclassified Radiologic Source Terms (Bowen et al., 1999) and taking into consideration radionuclide distribution between melt glass, rubble and groundwater (IAEA, 1998),  $^{237}\text{Np}$  appears to be substantially less mobile than tritium and other non-sorbing radionuclides, as expected. However, this analysis also suggests that  $^{237}\text{Np}$  mobility is surprisingly similar to that of plutonium. The similar transport behavior of Np and Pu can be explained by one of two possibilities: (1) Np(IV) and Pu(IV) oxidation states dominate under mildly reducing NNSS groundwater conditions resulting in similar transport behavior or (2) apparent Np transport is the result of transport of its parent  $^{241}\text{Pu}$  and  $^{241}\text{Am}$  isotopes and subsequent decay to  $^{237}\text{Np}$ . Finally, measured  $^{237}\text{Np}$  concentrations were compared to recent Hydrologic Source Term (HST) models. The  $^{237}\text{Np}$  data collected from three wells in Frenchman Flat (RNM-1, RNM-2S, and UE-5n) are in good agreement with recent HST transport model predictions (Carle et al., 2005). The agreement provides confidence in the results of the predictive model. The comparison to Cheshire HST model predictions (Pawloski et al, 2001) is somewhat ambiguous due to the low concentration resolution of the particle transport model.

## Introduction

Among all the Np isotopes,  $^{237}\text{Np}$ , an alpha-particle emitter with a half-life of 2.14 million years, is the most stable and long-lived. At the NNSS, the main sources of  $^{237}\text{Np}$  are nuclear device source material (radiochemical tracer) and the decay products of  $^{237}\text{U}$ ,  $^{241}\text{Pu}$  and  $^{241}\text{Am}$  (Bowen 2001, Smith et al. 2003). The most common oxidation state of  $^{237}\text{Np}$  in natural oxic waters is expected to be +5 (as  $\text{NpO}_2^+$ ), which sorbs relatively weakly to minerals and other organic and inorganic ligands (Choppin 2006, Assinder et al. 1991, Assinder 1999, Kenna and Sayles 2002, Kenna 2009). Thus, among the actinides, it is expected that Np should be far more mobile than Pu and Am (Lindahl et al. 2005, Yamamoto et al. 1991).  $^{237}\text{Np}$  was identified in the proposed Yucca Mountain repository total system performance assessment to be a key long-term dose contributor due to its long half life and relatively high solubility in the assumed oxygenated

environment. By analogy,  $^{237}\text{Np}$  may also play a role in contaminant boundary estimates at the NNSS.

Only a limited number of Np measurements have been reported for NNSS “hot wells” (radiologically contaminated groundwater wells). Most of these reported values are near instrument detection limits (Finnegan and Thompson 2002), which can lead to large measurement uncertainties. These large uncertainties limit our ability to interpret Np transport behavior and calibrate or validate reactive transport models. For example, at the Cambric site (Figure 1), reported  $^{237}\text{Np}$  concentrations at RNM-1 (Cambric cavity well), RNM-2S (satellite pumping well), and UE-5n (satellite well which intercepted contamination from recharging RNM-2S water) were  $3 \times 10^{-13}$  mol/L for all three wells, with a method detection limit on the order of  $10^{-14}$  mol/L (estimated). Cambric Hydrologic Source Term (HST) reactive transport models predicted  $\sim 10^{-13}$  mol/L at RNM-1,  $\sim 10^{-15}$  mol/L at RNM-2S, and little or no Np at UE-5n (Carle, et al., 2005). It is not clear whether the differences between measured and predicted values can be attributed to measurement uncertainty or inaccurate model predictions. A disagreement also exists between predicted and reported  $^{237}\text{Np}$  concentrations from the Cheshire post-shot hole (U-20n PS#1 DD) (Figure 2). Clearly, validation of modeling results requires more accurate measurement of  $^{237}\text{Np}$  concentration. Reliable and high-quality data are needed to effectively compare model results to  $^{237}\text{Np}$  concentrations in groundwater.

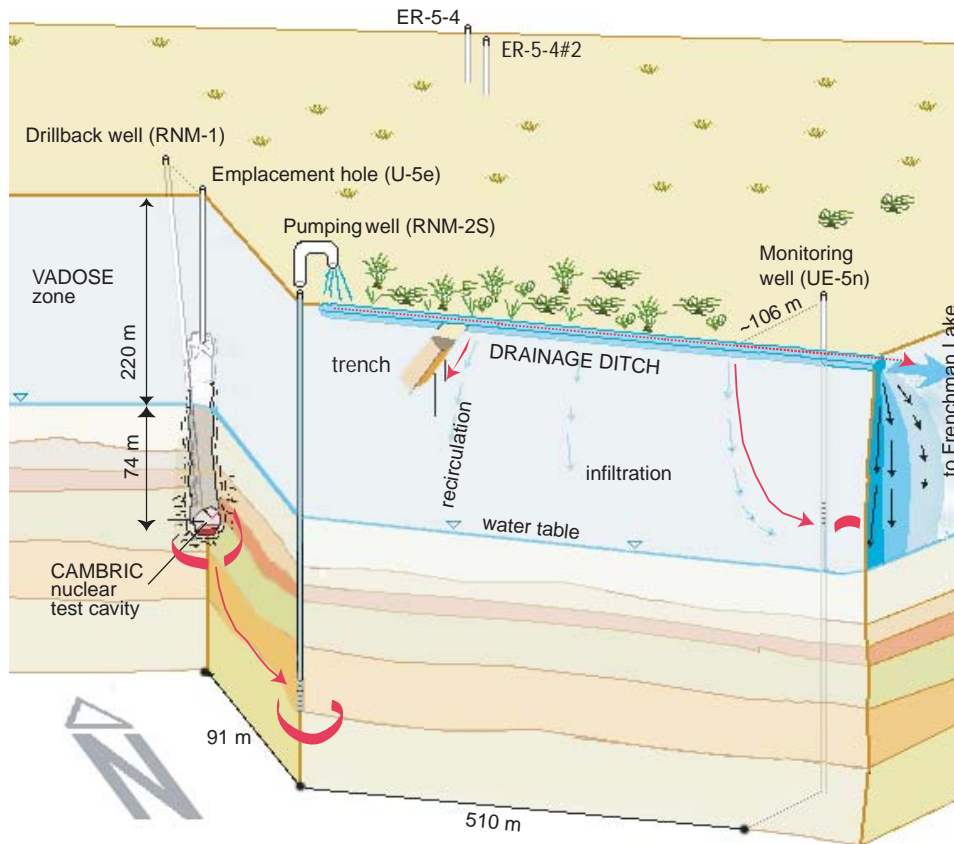


Figure 1. A view of the Cambric site with associated groundwater sampling wells (RNM-1, RNM-2S, and UE-5n) and their locations. From Carle et al. (2005).

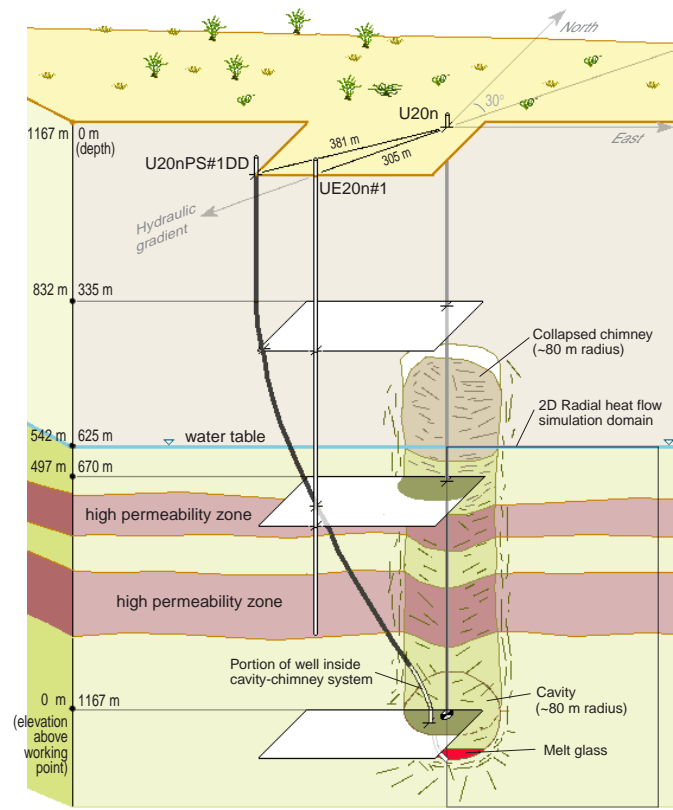


Figure 2. A view of the Cheshire site with associated groundwater sampling wells (U-20n PS#1 DD and UE-20n#1) and their locations. Well UE-20n#1 has not been sampled recently due to pump failure. From Pawloski et al. (2001).

Major challenges in the analysis of  $^{237}\text{Np}$  in environmental samples are its ultra low concentration and lack of a suitable yield tracer. Primary techniques used for determination of  $^{237}\text{Np}$  in environmental samples are alpha spectrometry (Gue´rin 2010, Harvey and Thurston 1988, Lindahl 2004, Prosser et al. 1994, Rosner et al. 1993, Yamamoto et al. 1991), neutron activation analysis (Kalmykov et al. 2004) and the most frequently used ICP-MS (Gue´rin et al. 2010, Kuczewski et al. 2003, Lindahl et al. 2005, Röllin et al. 2009, Truscitt et al. 2001). Other sensitive methods, such as TIMS (Beasley et al. 1998), AMS (Keith-Roach et al. 2001, Wang et al. 2010) and luminescence (Ivanova et al. 1994, Novikov et al. 2009) have also been reported. The advantages of using ICP-MS are high accuracy, speed, and sensitivity, as well as the simultaneous measurement of multiple isotopes. Although isobaric interferences from uranium hydrides such as  $^{235}\text{U}^1\text{H}_2^+$ ,  $^{236}\text{U}^1\text{H}^+$  have been reported (Heras et al. 2002), the most frequently observed interference is the peak tailing (also known as abundance sensitivity) of  $^{238}\text{U}$ . Therefore, a sufficient separation of the uranium from  $^{237}\text{Np}$  is always desired for mass spectrometric analysis. Radionuclide measurement techniques for environmental samples have been reviewed in depth by several authors in recent years (Vajda and Kim 2011, Hou and Roos 2008, Ketterer and Szechenyi 2008, Lariviere et al. 2006).

Suitable yield tracers for  $^{237}\text{Np}$  are limited to  $^{235}\text{Np}$  (half-life of 396 days, Harvey and Sutton 1987),  $^{236}\text{Np}$  (half-life of 154000 years, Efurud et al. 1986, Beasley et al. 1998, Kenna and Sayles 2002, Kenna 2009), and  $^{239}\text{Np}$  (half-life of 2.3 days). Given that isotopes of  $^{235}\text{Np}$  and  $^{236}\text{Np}$  are rare and not readily accessible, the most common yield tracer is the short-lived beta emitter  $^{239}\text{Np}$  (Lindahl et al. 2004, Lindahl et al. 2005, Röllin et al. 2009, Prosser 1994, Harvey and Thurston 1988, Yamamoto et al. 1991). The  $^{239}\text{Np}$  can be “milked” by separating it from its parent isotope  $^{243}\text{Am}$ . The activity of  $^{239}\text{Np}$  tracer can be determined using Gamma spectrometry or Liquid Scintillation Counting (LSC) while the  $^{237}\text{Np}$  concentration can be analyzed using ICP-MS.

In the present study, we set out to measure ultra low levels of  $^{237}\text{Np}$  in a number of ground water samples from hot wells at the NNSS. To achieve this goal, we first developed an effective procedure to separate and purify  $^{237}\text{Np}$  from 1 liter of groundwater. The  $^{239}\text{Np}$  tracer was used to quantify yield. The recent purchase of a state of the art magnetic sector ICP-MS provided the capability to measure  $^{237}\text{Np}$  at ultra-low levels ( $\sim 0.2$  parts per quadrillion ( $7 \times 10^{-16}$  mol/L) for a 1 L groundwater sample). The measured  $^{237}\text{Np}$  concentrations are first compared to Maximum Contaminant Levels established by the EPA for  $^{237}\text{Np}$  (15 pCi/L). The data are also compared to other radionuclides, such as  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{36}\text{Cl}$ ,  $^{129}\text{I}$ ,  $^{99}\text{Tc}$  and plutonium, in order to evaluate  $^{237}\text{Np}$  transport behavior relative to other radionuclides. Finally, the data are compared to recent HST reactive transport models (i.e. Carle et al., 2005; Pawloski et al., 2001) to evaluate the quality of model predictions.

## Experimental

### 1. Sample collection

Eight well samples and one tunnel water sample collected in recent years from all five corrective action units (CAU) at the NNSS were analyzed in the present study (Table 1). Of the samples measured, 5 are from near the working point of tests (Cheshire, Chancellor, Almendro, Dalhart, and Cambric (RNM-1)), three are located downstream of tests (ER-20-5#1, RNM-2S, UE-5n), and one is from a flooded tunnel (T tunnel). A map for the sampling locations is shown in Figure 3. All samples were collected via pumps or bailers directly into new 1L or 20 L plastic containers. The samples were all stored at room temperature at LLNL with no acidification. Samples were not acidified because of an interest in preserving the actinide associations with mineral colloids. However, for the  $^{237}\text{Np}$  analyses, 1 L containers (including colloidal constituents) were acidified prior to sample digestion and the empty sample bottles rinsed with concentrated  $\text{HNO}_3 + \text{HF}$  (5:1) to minimize potential loss of  $^{237}\text{Np}$  to container walls. For samples stored in 20 L containers, containers were shaken vigorously prior to removing 1 L samples for digestion and Np analysis; rinsing of containers was not performed, which leads to possible underestimates of Np concentration due to losses to container walls. This effect is discussed in detail in the text. Only total  $^{237}\text{Np}$  concentrations in groundwater (aqueous and colloid-associated) were investigated.

## 2. *Reagents and tracers*

Reagents used were analytical grade or better and used as received. De-ionized water with resistivity of 18.2 megaohm-cm from a Milli-Q Water (MQW) purification system was used in all procedures and solution preparations. NIST traceable SRM 4341  $^{237}\text{Np}$  standard was diluted and used for ICP-MS calibration. Anion exchange resin AG1x8 (chloride form, 50-100 and 100-200 mesh, Bio-Rad Laboratories) and UTEVA extraction resin (50-100 micron, Eichrom) was used for  $^{239}\text{Np}$  and  $^{237}\text{Np}$  separation and purification. AG resins were cleaned using HCl and MQW and UTEVA resins were cleaned using MQW prior to use. New Teflon jars/vials (Savillex) were boiled in 1:1  $\text{HNO}_3$  and Milli-Q water prior to use.

The  $^{239}\text{Np}$  isotope was milked from its parent nuclide  $^{243}\text{Am}$  and used as a chemical yield tracer for  $^{237}\text{Np}$  separation and purification. To purify the  $^{239}\text{Np}$ , the  $^{243}\text{Am}$  solution was dried and re-dissolved in <1 mL of conc. HCl and HI (50:1 v/v). The  $^{243}\text{Am}$  solution was warmed on a hotplate for 10 minutes to reduce  $^{239}\text{Np}$  to the +4 oxidation state prior to loading onto a purification column. The column was made from a 1 mL disposable transfer pipette plugged with a porous frit and AG1x8, 50-100 mesh resin. The loaded column was rinsed with 5 column volumes (cv) of conc. HCl + HI (50:1 v/v) and  $^{239}\text{Np}$  was eluted using 6 column volumes (cv) of 6 M HCl + 0.05 M HF. Two AG1x8 resin columns were used to ensure a complete separation of  $^{239}\text{Np}$  from its parent  $^{243}\text{Am}$ . This procedure was necessary to reduce and even eliminate positive errors in  $^{239}\text{Np}$  decay measurements from trace levels of  $^{243}\text{Am}$  over several half-lives of  $^{239}\text{Np}$ . The activities of  $^{239}\text{Np}$  were measured using gamma detector (Broad Energy Ge Detector (BEGe), Canberra). Energy branch at 277 keV was used to quantify  $^{239}\text{Np}$  and other energy branches such as 209, 228, 315 and 334 keV were used for  $^{239}\text{Np}$  quality control.

## 3. *Analytical methods*

A 1 liter groundwater sample in a Teflon (Savillex) jar was acidified with 10 mL conc. nitric acid and spiked with  $^{239}\text{Np}$  tracer with an activity of 3000 to 5000 dpm. The sample was gently heated on a hotplate and the sample allowed to evaporate. The resulting sample residue was repeatedly digested in concentrated HCl, aqua regia and/or hydrogen peroxide. If a full digestion could not be achieved, the remaining precipitate was repeatedly washed with concentrated HCl. In preparation for column purification, the digested sample was dissolved in 2 mL concentrated HCl+ HI (50:1 v:v) and warmed up on a hotplate for 10 min. to adjust the oxidation state of neptunium to Np(IV). An anion exchange resin column (2 mL AG1x8, 100-200 mesh Poly-prep column, BioRad) was preconditioned with Milli-Q water, conc. HCl, and conc. HCl+HI (50:1 v:v). The Np(IV) sample was loaded onto the column. Tetravalent Np and U were retained on the resin while trivalent Pu and most other impurities eluted. The loaded column was washed with 5 cv of conc. HCl+HI (50:1) and followed by Np elution using 6 cv of 6 M HCl+0.05 M HF (most of the U was retained on the column). Two columns of AG1x8 resin were used in Np separation. After 2 anion exchange columns, the Np in the eluent was dried 2-3 times in dilute nitric acid to oxidize Np to its +5 state. The sample residue was dissolved into 1 mL of 4 M  $\text{HNO}_3$  solution. If further purification of Np from uranium was necessary, the Np sample in 4M  $\text{HNO}_3$  solution was passed through a small UTEVA column (0.2 mL column bed made of a small disposable transfer pipet). The uranium was retained while Np(V) eluted. The

Np-containing eluent from the UTEVA column was dried on a hot-plate and the residue was redissolved in 1 mL of 2% HNO<sub>3</sub> as the final sample form. Two 1 mL samples of <sup>239</sup>Np spike solution were preserved without processing as gamma counting references for each batch of sample analyses. The activities of <sup>239</sup>Np in purified samples were measured by Gamma spectrometry, and compared with activities in reference samples to determine the <sup>237</sup>Np yield. After all <sup>239</sup>Np decayed away (~6 half-lives), the <sup>237</sup>Np concentrations was analyzed using a NuPlasma HR ICP-MS.

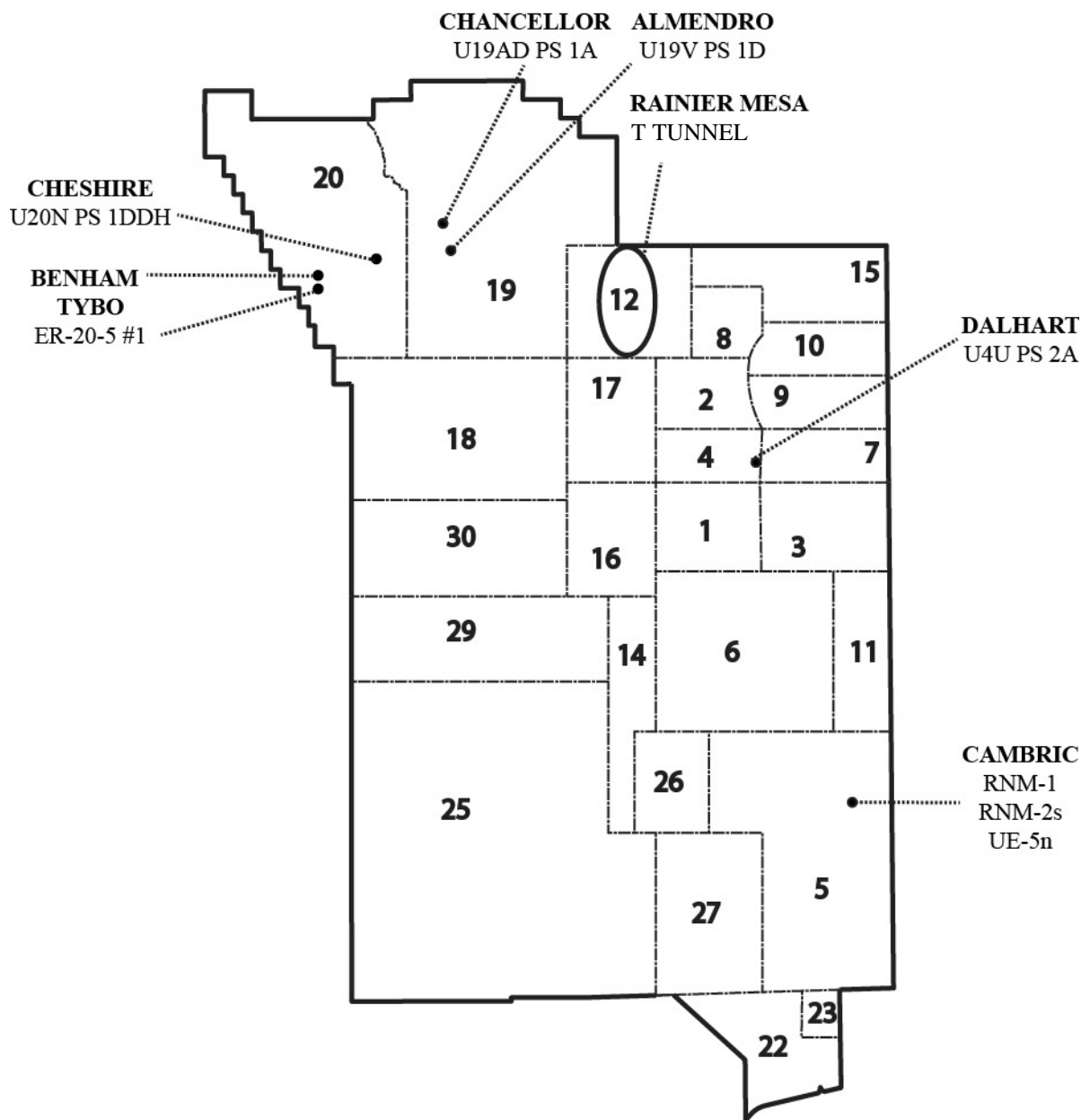


Figure 3. Map of NNSS and sampling locations.



## Results and Discussion

### 1. Separation and purification procedures

The  $^{243}\text{Am}$  “cow” which was used as a  $^{239}\text{Np}$  source contained ~ 10% (by activity) of  $^{241}\text{Am}$ , which decays to  $^{237}\text{Np}$ . Due to its long half-life,  $^{237}\text{Np}$  continues to accumulate in the  $^{243}\text{Am}$  “cow” while  $^{239}\text{Np}$  activity reaches secular equilibrium with  $^{243}\text{Am}$ . This results in an ever increasing  $^{237}\text{Np}/^{239}\text{Np}$  ratio as a function of time. As a result, the  $^{239}\text{Np}$  spike can introduce a significant amount of  $^{237}\text{Np}$  into samples and increase the background  $^{237}\text{Np}$  signal. In order to minimize the  $^{237}\text{Np}$  background in the  $^{239}\text{Np}$  spike solution, the  $^{243}\text{Am}$  stock solution was purified from  $^{237}\text{Np}$  using AG1x8 50-100 mesh resin 1-2 days prior to milking  $^{239}\text{Np}$ . The spiked activity was also limited to the lowest possible level that would accommodate the instrument detection limits. Based on the  $^{243}\text{Am}/^{241}\text{Am}$  isotope ratio of the  $^{243}\text{Am}$  “cow” and the two-day ingrowth time used, the amount of  $^{237}\text{Np}$  introduced into samples from the  $^{239}\text{Np}$  spike is  $< 5 \times 10^{-6}$  pCi/sample. In theory, the amount of  $^{237}\text{Np}$  introduced by the spike is the limiting factor for the procedure blank. To reduce  $^{237}\text{Np}$  background, simpler and quicker separation procedures combined with a more sensitive, yet accurate counting method is desirable. Alternatively, a stock solution with a higher  $^{243}\text{Am}/^{241}\text{Am}$  ratio should be used.

In  $^{237}\text{Np}$  analysis using ICP-MS, the major interference comes from the tailing of  $^{238}\text{U}$ , which is undoubtedly present at much greater quantities compared to  $^{237}\text{Np}$ . Therefore, a good chemical separation of  $^{238}\text{U}$  is required (Hou and Roos 2008). The NuPlasma magnetic sector, multi-collector HR ICP-MS can tolerate low ppb levels of  $^{238}\text{U}$  for quantitative measurements of  $^{237}\text{Np}$  at ppq levels. However, due to the interferences from unknown impurities in the groundwater samples, the AG1x8 resin column was insufficient to reduce uranium concentration to the desirable low ppb or sub ppb levels. Solvent extraction has been used in conjunction with anion exchange columns to achieve a better separation of Np from its interfering impurities (Efurd et al. 1986, Harvey and Thurston 1988) for sub-nanogram levels of  $^{237}\text{Np}$ . However, solvent extraction has not been applied to ultra trace Np separation. In our study, the AG1x8 column was followed by a UTEVA extraction resin column to effectively separate uranium from Np. A quadrupole ICP-MS was used to survey uranium concentrations in 5  $\mu\text{L}$  Np samples to ensure that sufficient removal of  $^{238}\text{U}$  was achieved. The typical overall Np chemical recovery yields among the samples ranged from 50% to 90%, which was considered acceptable for ultra low level analyses.

### 2. Neptunium data

The  $^{237}\text{Np}$  data are grouped by CAU and listed in Table 1. The detectable  $^{237}\text{Np}$  concentrations ranged from  $2.7 \times 10^{-5}$  in well RNM-1 (Cambrian cavity) to  $7.1 \times 10^{-2}$  pCi/L in well U-19ad PS1a (Chancellor cavity). The measured  $^{237}\text{Np}$  concentrations in all samples were well below the maximum contaminant level (MCL, 15 pCi/L) for alpha emitters identified by the U.S. EPA (2009). The Np concentrations in groundwater samples from Almendro (U-19v PS1ds) hot well and two Cambrian satellite wells (RNM-2s and UE-5n) were below our detection limit of  $1 \times 10^{-5}$  pCi/L. Duplicate samples were run at Cambrian (RNM-2s), Dalhart (U4u PS2a),

Chancellor (U19ad PS1a), and Almendro (U-19v PS1ds) and reproducible results within uncertainties of 10% or less (when detectable) were obtained.

Cheshire samples collected on 11/15/05 in two different containers analyzed in different batches differ by an order of magnitude. This may have been caused by the long storage times and the fact that the 20 L container from which one sample was taken was not acidified during sample processing. Loss of Np to container walls may have been a problem. Further investigation is needed to positively identify the cause. Analysis of acidified samples with shorter hold times is always preferable.

Regardless of sampling location, all samples except the high concentration Cheshire sample resulted in  $^{237}\text{Np}$  concentrations up to 3 orders of magnitude lower than the previously reported values (Finnegan and Thompson, 2002). The  $^{237}\text{Np}$  data previously reported was obtained from groundwaters sampled at the same locations but on different dates. Nevertheless, the differences between these two sets of data suggest the existence of a systematic potential error in historical data.

The RNM-1  $^{237}\text{Np}$  data obtained in the present study was about an order of magnitude lower than the Np concentrations predicted in HST models ( $1.5 \times 10^{-4}$  pCi/L, Carle et al. 2005). Uncertainties in the radiologic source term (based on an average source term for all tests in Frenchman Flat from Bowen et al., 2001), in the partitioning behavior of Np (IAEA, 1998), and in nuclear melt glass dissolution which releases Np into groundwater are likely to limit accuracy of unclassified source term models to within an order of magnitude or larger. Thus, the measured values at RNM-1 should be considered in good agreement with model predictions. Modeling results also suggested that insignificant concentrations of  $^{237}\text{Np}$  would reach the RNM-2s and UE-5n wells, which is consistent with the non-detectable levels determined in our analyses.

The Np concentrations in groundwater from the cavity/chimney area of the Cheshire test were found to be  $3 \times 10^{-4}$  and  $6 \times 10^{-3}$  pCi/L in two separate analyses. As stated earlier, the relatively large difference between the two analyses may be the result of losses of Np to container walls during the long sample storage time, particularly for the sample stored in the 20L container which was not acidified. The Np concentration previously reported was  $3 \times 10^{-2}$  pCi/L, substantially higher than the values measured in this analysis. HST modeling (Pawloski et al., 2001) using particle transport methods did not accurately resolve Np distribution at low concentrations; Np concentrations in the cavity chimney 23.5 years after the test ( $t_0 = 1976$ ) were predicted to range from  $10^{-8}$  mol/L (1600 pCi/L) in the glass zone to below  $10^{-13}$  mol/L (0.02 pCi/L) in the upper cavity and chimney. The high  $^{237}\text{Np}$  concentration predicted for the glass zone are the result of simulated glass dissolution rates which were later found to be too high (Carle et al., 2005). The measured  $^{237}\text{Np}$  concentrations in the cavity chimney area are in qualitative agreement with predicted values for the upper cavity and chimney zones. However, the poor resolution of Np concentrations and various assumptions included in the model limits the applicability of this comparison.

Table 1. <sup>237</sup>Np, <sup>3</sup>H and total Pu activities in NNSS Groundwater Samples (all data were decay corrected to 9/23/92)

CAU <sup>1</sup>	Test Name	Sampling well/Location	Sampling date	This method		Previously Reported Value			
				<sup>237</sup> Np	+/-	<sup>237</sup> Np	<sup>3</sup> H	Pu-total	
				----- pCi/L -----					
Central Pahute Mesa	Almendro	U-19v PS1ds; Cavity/chimney	4/18/2006	< 1E-5		-	2.32E8	<0.004	
			4/18/2006	< 1E-5		-	2.32E8	<0.004	
			8/17/1999	-		< 0.0108	2.18E8	9.5	
	Camembert	U-19q PS1d; Chimney	10/20/1998	-		0.0216	2.94E7	0.019	
	Chancellor	U19ad PS1A; Cavity	5/1/2008	7.1E-2	1E-3	-	3.09E7	23.5	
			5/1/2008	7.0E-2	1E-3	-	3.09E7	23.5	
	Cheshire	U-20n PS1ddh; Cavity	11/15/2005	3.3E-4 <sup>2</sup>	3E-6	-	6.98E7	0.46	
11/15/2005			5.5E-3 <sup>3</sup>	3E-5	-	6.98E7	0.46		
10/12/1999			-		0.027	7.58E7	0.51		
Western Pahute Mesa	Tybo/Benham	ER-20-5 #1; 280/1300 m from Tybo/Benham	11/30/2004	3.3E-4	1E-6	-	7.48E7	0.42	
		ER-20-5 #3; 280/1300 m from Tybo/Benham	7/09/1998	-		0.149	8.60E7	0.59	
			4/30/1998	-		0.0211	2.14E5	NA	
Ranier Mesa	Hot Tunnels	U-12t gas sealed plug	11/2/2006	3.3E-4	3E-6	-	1.06E8	54	
Yucca Flat	Dalhart	U-4u PS2a; Chimney	2/6/2008	6.6E-5	3E-7	-	5.71E7	0.19	
			2/6/2008	5.9E-5	5E-7	-	5.71E7	0.19	
Frenchman Flat	Cambric	RNM-1, cavity	3/6/2007	2.7E-5	1E-6	-	1.95E3	0.006	
			6/28/2000	-		0.054	4.40E4	NA	
		RNM-2s; 91 m from Cambric	3/7/2007	< 1E-5		-	2.26E5	<0.02	
			3/7/2007	< 1E-5		-	2.26E5	<0.02	
				6/14/2000	-		0.054	2.93E5	NA
		UE-5n; 510 m from RNM-2s		2/12/2004	< 1E-5		-	2.79E5	<0.02
	4/19/2001		-		0.054				

<sup>1)</sup> CAU: Corrective Action Unit

<sup>2)</sup> Groundwater sample stored in 20-liter container prior to analysis.

<sup>3)</sup> Groundwater sample stored in 1-liter container.

### 3. Neptunium transport behavior

As an anthropogenic radionuclide, the main sources of  $^{237}\text{Np}$  at NNSS are from the original test-derived source material and as a decay product of short lived  $^{237}\text{U}$ , which was produced through neutron capture reactions of device components  $^{235}\text{U}$  and  $^{236}\text{U}$  (Bowen 2001, Smith et al. 2003). The  $^{237}\text{Np}$  is also produced via the  $^{241}\text{Am}$  and  $^{241}\text{Pu}$  decay chain. Previous studies of environmental transport of  $^{237}\text{Np}$  have shown that the mobility of  $^{237}\text{Np}$  conspicuously depended on its speciation and redox conditions of the surroundings (Dozol and Hagemann 1993, Choppin 2006). Neptunium was found to be very mobile in surface waters such as Irish Sea (Assinder 1999), Lake Karachai (Novikov et al. 2009) and Swedish-Danish waters (Lindahl et al. 2005) due to the oxygenated water conditions. Even if the initial distribution of Np is similar, if not the same, as Pu, the former radionuclide tends to become pentavalent and mobile as it migrates away from its origins over time (Lindahl et al. 2004& 2005, Novikov et al. 2009). The groundwater conditions in NNSS hot wells are relatively isolated and the redox conditions can vary (Hu et al. 2008, Nimz and Thompson 1992). As a result, oxidizing conditions cannot be assumed for all NNSS groundwaters. Thus, we cannot assume that  $^{237}\text{Np}$  transport behavior will be governed by the behavior of the oxic +5 cation.

Activity ratios can be used to evaluate the mobility of Np relative to other radionuclides. For example, if the ratio of Np to a non-sorbing tracer in the mobile phase is low relative to its initial source term ratio, it suggests that Np is retarded or otherwise immobilized. However, in the case of underground nuclear tests, one must also take into account that a fraction of initial source term will be deposited in nuclear melt glass, effectively isolating it from groundwater. The IAEA (1998) has published partitioning estimates (i.e. estimates of groundwater accessible source terms) for many radionuclides associated with underground nuclear tests. Thus, we can compare isotope ratios relative to the expected groundwater-accessible radionuclide ratios using the following equation:

$$R = \frac{\left(\frac{^{237}\text{Np}}{\text{RN}}\right)_{\text{measured}}}{\left(\frac{^{237}\text{Np}}{\text{RN}}\right)_{\text{source}} \times \left(\frac{f_{^{237}\text{Np}}}{f_{\text{RN}}}\right)_{\text{IAEA}}}$$

where  $^{237}\text{Np}$  and RN are the measured concentration and source term (Bowen et al. (2001)) inventory of  $^{237}\text{Np}$  and reference radionuclide in a particular hot well and CAU, respectively, and  $f$  is the fraction of the inventory that is groundwater accessible based on IAEA (1998). The fraction that is groundwater accessible is 100% for tritium and  $^{14}\text{C}$ , 50% for  $^{36}\text{Cl}$  and  $^{129}\text{I}$ , 20% for  $^{99}\text{Tc}$ , and 5% for  $^{237}\text{Np}$ , and 2% for Pu. If the ratio, R, is less than 1, it indicates a relatively smaller fraction of neptunium in the mobile phase relative to the reference radionuclide (i.e.  $^{237}\text{Np}$  depletion). The uncertainty in the source term and groundwater accessible fraction limit the efficacy of this comparison. Nevertheless, values  $\ll 1.0$  indicate that Np is substantially depleted relative to the reference radionuclide. In most cases, this depletion can be attributed to its greater sorption (lower mobility) relative to the reference radionuclide.

Figure 4 is a plot of activity ratio of  $^{237}\text{Np}$  relative to  $^3\text{H}$  as a function of tritium concentration for all wells with detectable  $^{237}\text{Np}$  concentrations. In all cases, tritium has been decay corrected to September 23, 1992, as reported in Bowen et al. (2001). For reference, we also identify the Maximum Contaminant Level as defined by the EPA (2009) for tritium. As stated earlier, all  $^{237}\text{Np}$  concentrations are well below the MCL for that radionuclide. However, most samples are well above the MCL for tritium (20,000 pCi/L). Importantly, the R values for all hot well samples except RNM-1 in Frenchman Flat are  $\ll 1$ , suggesting that Np is much less mobile than  $^3\text{H}$ . Well RNM-1 is unique in that nearly all the  $^3\text{H}$  was pumped out of the cavity during the course of a 20 year pumping experiment at RNM-2s (Bryant 1992, Nimz and Thompson 1992). At RNM-1, the relatively high  $^{237}\text{Np}$  concentrations relative to tritium results from the fact that the source term tritium has been effectively removed from the cavity while  $^{237}\text{Np}$  has not.

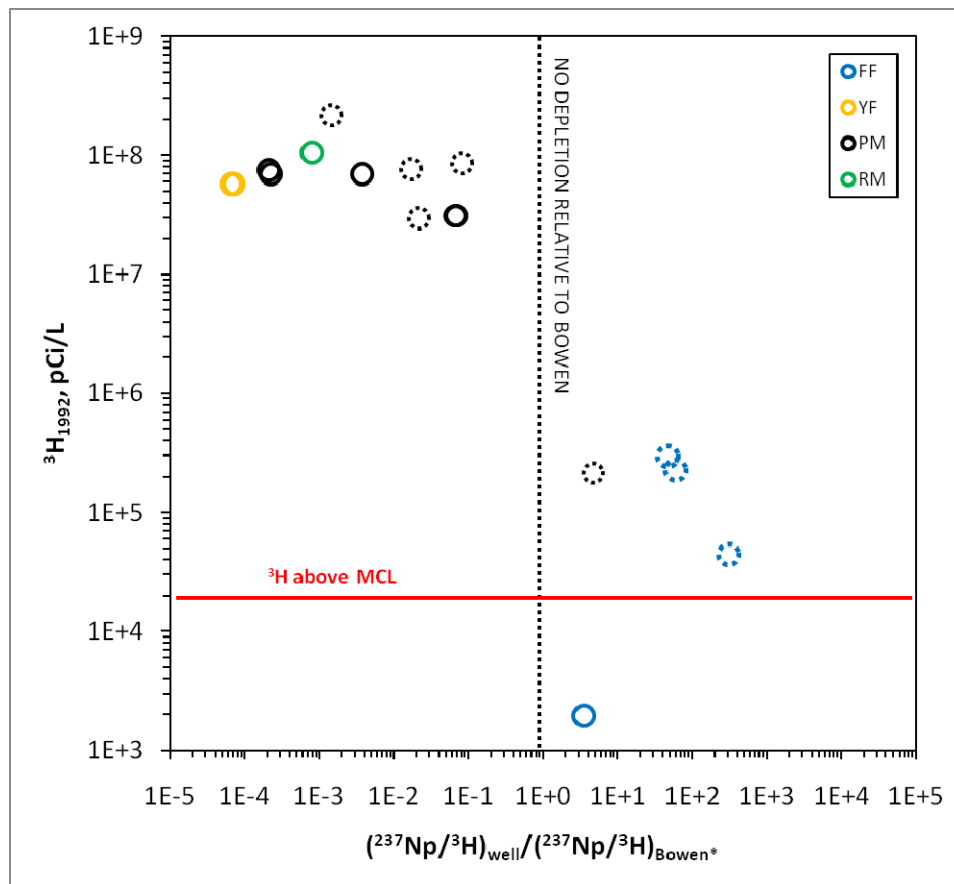


Figure 4.  $^{237}\text{Np}/^3\text{H}$  isotope ratio in groundwater relative to source term ratio based on Bowen et al. (2001) and IAEA (1998). Values  $\ll 1$  are indicative of retardation. FF data point is from well RNM-1. Dashed circles represent historical data from the UGTA geochemistry database. Color scheme indicates the CAU of sampled well locations with: 1) FF = Frenchman Flat, 2) YF = Yucca Flat, 3) PM = Pahute Mesa, 4) RM = Ranier Mesa.

The data in Figure 4 clearly indicate that  $^{237}\text{Np}$  is retarded relative to  $^3\text{H}$ . We can qualitatively simulate the effect of retardation in the cavity/chimney of a test by fitting a Continuous Stirred-Tank Reactor (CSTR) model to the cavity/chimney hot well samples observational data. The model treats the cavity/chimney system as an equilibrium CSTR for which the concentration evolution of each radionuclide is predicted by the following equation:

$$C_i = C_0 \times e^{\left(\frac{J \times t}{R \times V}\right)}$$

where the concentration of species  $i$  is a function of the initial aqueous concentration ( $C_0$ ), the groundwater flux ( $J$ ), time ( $t$ ), retardation ( $R$ ), and reactor volume ( $V$ ). For this model, an average radionuclide initial concentration in the cavity/chimney region was calculated based on the total radiologic inventory for each CAU (Bowen et al., 2001), the sum of all exchange volumes for each test calculated using the following:  $70.2 * Y^{1/3} / [\rho_{ob} * WP]^{1/4}$  (Pawloski, 1999) where  $Y$  is the announced yield or maximum of announced yield range from DOE/NV-209 rev.15 (2000) (kt),  $\rho_{ob}$  is an approximate overburden density ( $2.0 \text{ Mg/m}^3$ ), and  $WP$  is the working point depth (meters). The exchange volume was assumed to be spherical with a radius of  $1.5 R_c$ , fully saturated, and with a porosity of 30%. The groundwater accessible fraction was based on IAEA (1998) partitioning estimates.

Figure 5 compares the cavity/chimney data to CSTR model predictions based on a retardation factor ( $R$ ) of 1000 which is equivalent to a  $K_d$  of 170 mL/g. The CSTR model produces a straight line on a log-log plot which represents the decrease in tritium concentration and the increase in the  $^{237}\text{Np}/^3\text{H}$  isotope ratio over time. The qualitative match to the data suggests that effective  $K_d$ s for Np lie broadly in a range from 10 mL/g to values  $>100 \text{ mL/g}$ . These retardation values are higher than typically reported for Np sorption to tuff and alluvium (YMP, 2004). Most likely, they reflect conservative estimates of Np partitioning to groundwater, variability between individual test radiologic source terms, and processes other than sorption (e.g. coprecipitation/sequestration of Np in secondary mineral phases). Regardless of the processes involved, the modeling results indicate that overall Np retardation appears to be substantial and provides an explanation for the low  $^{237}\text{Np}$  concentrations observed in hot well cavity/chimney samples (the source of radiologic contamination from underground nuclear testing). We do not anticipate that  $^{237}\text{Np}$  concentrations will evolve over time to approach concentrations that would surpass MCL limits identified by the EPA (2009) for alpha-emitting radionuclides.

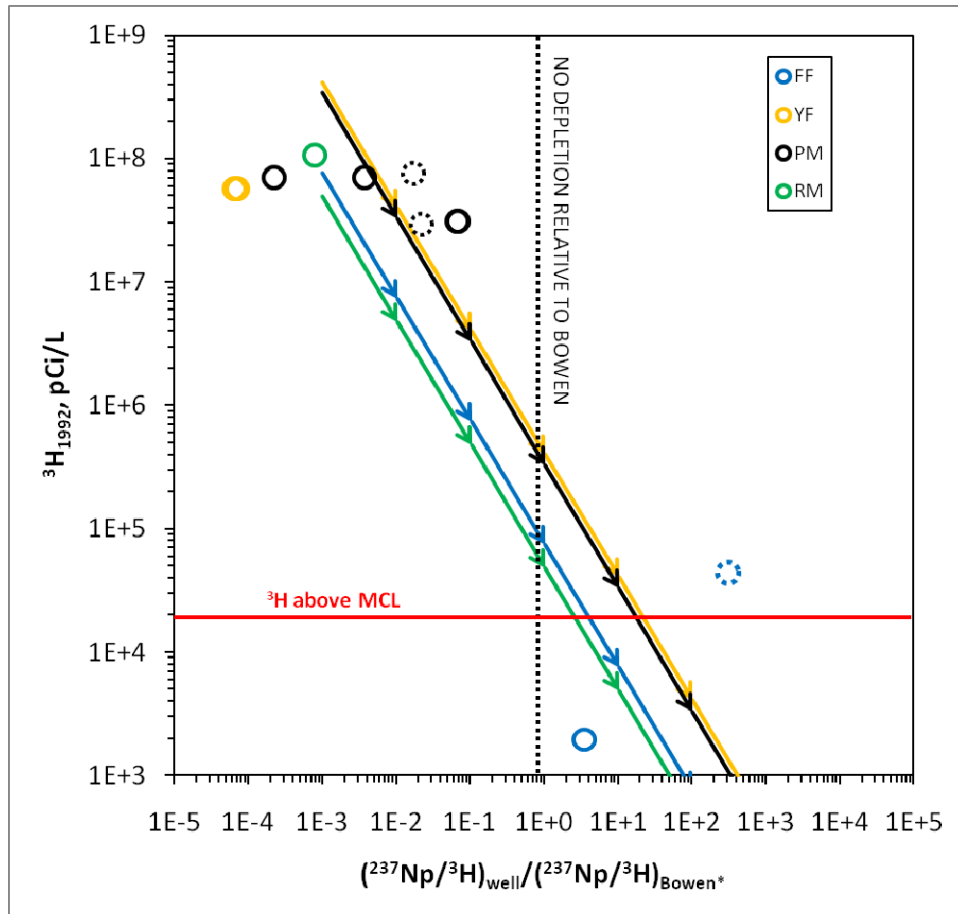


Figure 5.  $^{237}\text{Np}/^3\text{H}$  isotope ratio in cavity/chimney groundwater samples relative to initial ratio based on Bowen et al. (2001) and IAEA (1998) and comparison to model prediction of CSTR with a retardation factor of 1000 (lines and arrows represent CSTR-predicted evolution of isotope ratio in the cavity as a result of groundwater flow). Dashed circles represent historical data from the UGTA geochemistry database. Color scheme indicates the CAU of sampled well locations with: 1) FF = Frenchman Flat, 2) YF = Yucca Flat, 3) PM = Pahute Mesa, 4) RM = Ranier Mesa.

Figure 6 contains plots of activity ratios of  $^{237}\text{Np}$  to other presumed mobile radionuclides ( $^{14}\text{C}$ ,  $^{36}\text{Cl}$ ,  $^{99}\text{Tc}$  and  $^{129}\text{I}$ ). The results compare favorably with the tritium ratios, suggesting that  $^{237}\text{Np}$  in the analyzed NNSS hot wells is generally less mobile than the commonly considered non-sorbing radionuclides. Importantly, historical  $^{237}\text{Np}$  concentration measurements are consistently higher than those measured here, possibly resulting from the higher detection limits or other artifacts. In some cases (e.g.  $^{36}\text{Cl}$  data), this results in an apparent Np mobility that is greater than non-sorbing radionuclides (ratio  $\gg 1$  in high activity samples).  $^3\text{H}$  and  $^{36}\text{Cl}$  have been shown to exhibit unretarded migration over a wide range of environmental conditions (Hu et al. 2008). Thus, the greater mobility of  $^{237}\text{Np}$  compared to  $^{36}\text{Cl}$  is unlikely. While  $^{14}\text{C}$ ,  $^{129}\text{I}$  and  $^{99}\text{Tc}$  can exhibit some retardation depending upon the type of geological media and redox conditions of their surroundings (Hu et al. 2008), it appears that  $^{237}\text{Np}$  is relatively less mobile than these radionuclides. Importantly, the uncertainties and assumptions made in calculating these ratios lend themselves to only a qualitative assessment of the relative mobility of  $^{237}\text{Np}$ .

Figure 7 shows relative mobility of neptunium to total plutonium in the studied wells. Surprisingly, the ratios are centered near 1 for most hot well data, suggesting that neptunium mobility is similar to plutonium at these locations. The historical data appear to be biased towards greater Np mobility. The observations are suggestive of two possible transport phenomena: 1) the predominance of Np(IV) in the mildly reducing groundwater conditions exhibits transport behavior similar to Pu(IV) or 2) an apparent transport of Np is the result of transport of its parent  $^{241}\text{Pu}$  and  $^{241}\text{Am}$  isotopes and subsequent decay to  $^{237}\text{Np}$ . In the first case, Np and Pu transport behavior is similar because both actinides are predominantly in the +4 state and exhibit similar sorption/retardation. In the second case, observed  $^{237}\text{Np}$  is a product of the decay of  $^{241}\text{Pu}$  and  $^{241}\text{Am}$  which have similar transport behaviors as other Pu isotopes ( $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ ). The available data cannot be used to distinguish between these two possibilities. The high ratio observed at RNM-1 suggests that oxygenated waters introduced into the cavity/chimney as a result of  $\sim 20$  years of pumping at this location may have remobilized Np by oxidizing it to Np(V). However, this explanation is not unique and other hypotheses may be equally plausible.



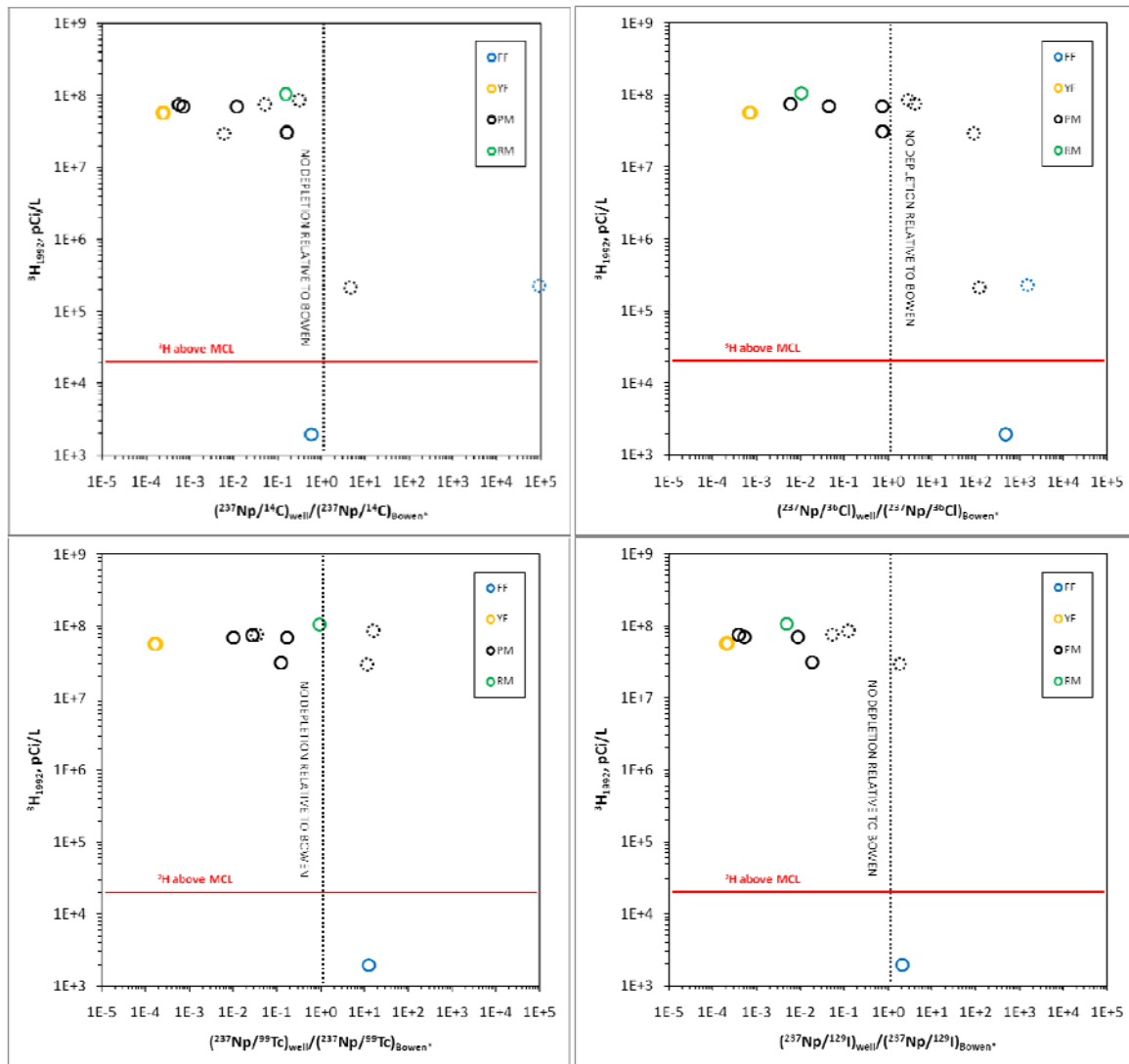


Figure 6. Isotope ratios of  $^{237}\text{Np}/^{14}\text{C}$ ,  $^{237}\text{Np}/^{36}\text{Cl}$ ,  $^{237}\text{Np}/^{99}\text{Tc}$ , and  $^{237}\text{Np}/^{129}\text{I}$  in groundwater relative to initial ratio based on Bowen et al. (2001) and IAEA (1998). Values  $\ll 1$  are indicative of retardation. Dashed circles represent historical data from the UGTA geochemistry database. Color scheme indicates the CAU of sampled well locations with: 1) FF = Frenchman Flat, 2) YF = Yucca Flat, 3) PM = Pahute Mesa, 4) RM = Ranier Mesa.

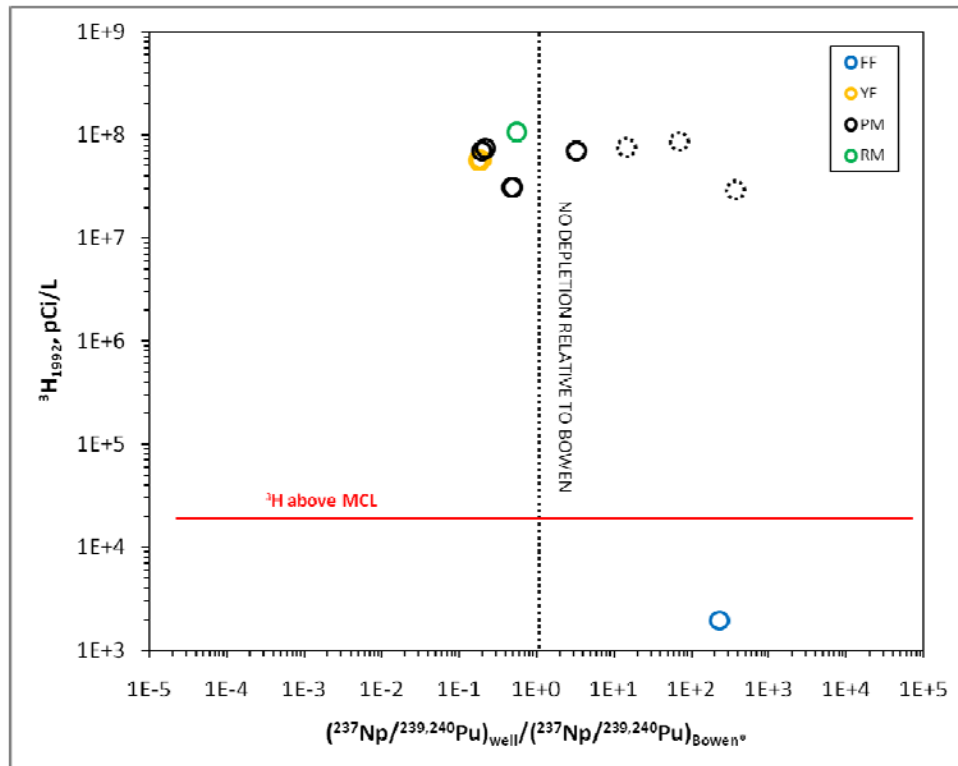


Figure 7. Isotope ratios of  $^{237}\text{Np}/^{239,240}\text{Pu}$  in groundwater relative to initial ratio based on Bowen et al. (2001) and IAEA (1998). Dashed circles represent historical data from the UGTA geochemistry database. Color scheme indicates the CAU of sampled well locations with: 1) FF = Frenchman Flat, 2) YF = Yucca Flat, 3) PM = Pahute Mesa, 4) RM = Ranier Mesa.

## Conclusions

We have successfully measured ultra trace levels of  $^{237}\text{Np}$  in groundwater samples collected from NNSS hot wells and tunnels in five different CAUs using an isotope dilution method. A short lived  $^{239}\text{Np}$  yield tracer in conjunction with a state of the art magnetic sector HR ICP-MS were used for the  $^{237}\text{Np}$  analyses. The measured  $^{237}\text{Np}$  concentrations in all samples were below the maximum contaminant level (MCL) of  $^{237}\text{Np}$  proposed for drinking water by the U.S. EPA (2009). The analyses of transport behavior of  $^{237}\text{Np}$  in these NNSS groundwaters suggest that  $^{237}\text{Np}$  was substantially less mobile than tritium and other conservative nuclides as expected. Surprisingly, its mobility appeared to be similar to that of plutonium ( $^{239,240}\text{Pu}$ ) either as a result of its reduction to Np(IV) and chemical similarity to Pu(IV) or as an artifact of its ingrowth from parent  $^{241}\text{Pu}$  and  $^{241}\text{Am}$ .

The measured  $^{237}\text{Np}$  concentrations by the present work were generally lower than previously reported. The difference may be, in part, a result of the high detection limits in historical data. However, additional data collection activities are needed to verify and quantify the measurement uncertainties and variabilities reported here.

The measured  $^{237}\text{Np}$  concentrations in Cambrian and Cheshire hot wells were compared to recent HST modeling efforts. The RNM-1  $^{237}\text{Np}$  data obtained in present study, about an order of magnitude lower than the values predicted by HST transport modeling ( $1.5 \times 10^{-4}$  pCi/L, Carle et al., 2005), is considered an acceptable validation of HST transport models. Modeling results also suggested that insignificant concentrations of  $^{237}\text{Np}$  would reach the RNM-2s and UE-5n wells, which is consistent with the non-detectable levels determined in our analyses. At the Cheshire site, HST modeling (Pawloski et al., 2001) using particle transport methods did not accurately resolve Np distribution at low concentrations; Np concentrations in the cavity chimney 23.5 years after the test ( $t_0 = 1976$ ) were predicted to range from 1600 pCi/L in the glass zone to below 0.02 pCi/L in the upper cavity and chimney. The high  $^{237}\text{Np}$  concentration predicted for the glass zone is the result of very high simulated glass dissolution rates. The measured  $^{237}\text{Np}$  concentrations in the cavity chimney area ( $3 \times 10^{-4}$  and  $6 \times 10^{-3}$  pCi/L) are in qualitative agreement with predicted values for the upper cavity and chimney zones. However, the poor resolution of Np concentrations and various assumptions included in the model limits the applicability of this comparison. While  $^{237}\text{Np}$  remains an important indicator for radionuclide transport rates at the NNSS, it does not appear to pose a significant hazard in relation to U.S. EPA maximum contaminant levels for alpha-emitting radionuclides.

## Acknowledgements

This work was funded by the Underground Test Area Project, National Nuclear Security Administration, Nevada Site Office and was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Security, LLC under Contract DE-AC52-07NA27344.

## References

- Assinder, D. J. 1999 A review of the occurrence and behaviour of neptunium in the Irish Sea. J. Environ. Rad. 44, 335-347
- Assinder, D. J., Yamamoto, M., Kim, C. K., Seki, R., Takaku, Y., Yamauchi, Y., Komura, K., Ueno, K., Bourne, G. S. 1991. Neptunium in intertidal coastal and estuarine sediments in the Irish Sea. J. Environ. Radioactivity 14, 135-145
- Beasley, T. M., Kelley, J. M., Maiti, T. C., Bond, L. A. 1998.  $^{237}\text{Np}/^{239}\text{Pu}$  atom ratios in integrated global fallout: a reassessment of the production of  $^{237}\text{Np}$ . Journal of Environmental Radioactivity, Volume 38, Issue 2, Pages 133-146
- Betti, M., Aldave de las Heras, L. 2004. Glow discharge spectrometry for the characterization of nuclear and radioactively contaminated environmental samples. Spectrochimica Acta Part B: Atomic Spectroscopy, Volume 59, Issue 9, Pages 1359-1376
- Bowen, S. M., 2001. Nevada Test Site Inventory, 1951-1992. LA-13859-MS, Los Alamos National Laboratory.
- Bryant, E. A. 1992. The Cambic Migration Experiment-A Summary Report. LA-12335-MS, Los Alamos National Laboratory.
- Carle, S.F., R. M. Maxwell, G. A. Pawloski, D. E. Shumaker, A. F. B. Tompson, M. Zavarin, 2005. Evaluation of the Transient Hydrologic Source Term for the Cambic Underground Nuclear Test at Frenchman Flat, Nevada Test Site" UCRL-TR-226916, Lawrence Livermore National Laboratory.
- Choppin, G. R., 2006. Actinide Speciation in Aquatic Systems. Mar. Chem., 99, 83.
- Dozol, M. and Hagemann, R. 1993. Radionuclide migration in the groundwaters: Review of the behavior of actinides. Pure & Appl. Chem. 65 (5), 1081-1102.
- Efurd, D. W., Drake, J., Roensch, F. R., Cappis, J. H., Perrin, R. E. 1986. Quantification of neptunium by isotope dilution mass spectrometry. LA-10701-MS, Los Alamos National Laboratory.
- EPA 2009. National Primary Drinking Water Regulations. EPA 816-F-09-0004, May 2009.
- Finnegan, D. L., Thompson, J. L. 2002. Laboratory and Field Studies Related to Radionuclide Migration at the Nevada Test Site in Support of the Underground Test Area Program and Hydrologic Resources Management Project," LANL-Report L A-13919-MS Los Alamos National Laboratory.
- Froidevaux, P., Bochud, F., Haldimann, M. 2010. Retention half times in the skeleton of plutonium and  $^{90}\text{Sr}$  from above-ground nuclear tests: A retrospective study of the Swiss population. Chemosphere, Volume 80, Issue 5, Pages 519-524
- Gue'rin, N., Langevin, M.A., Nadeau, K., Labrecque, C., Gagne, A., Larivi, D., 2010. Determination of neptunium in environmental samples by extraction chromatography after valence adjustment. Applied Radiation and Isotopes 68, 2132-2139.

- Harvey, B. R., Sutton, G. A., 1987. The use of  $^{235}\text{Np}$  as a yield tracer. Nucl. Instrum. Meth. Phys. Res. A254, 172-187.
- Harvey, B. R., Thurston, L. M. 1988. Analytical procedures for the determination of neptunium radionuclides in marine waters, sediments and biota. Aquat. Environ. Prot.: analyt. Meth., MAFF Direct. Fish. Res., Lowestoft, (1) p37.
- Heras, L. A., Hrnccek, E., Bildstein, O., Betti, M. 2002. Neptunium determination by dc glow discharge mass spectrometry (dc-GDMS) in Irish Sea sediment samples. J. Anal. At. Spectrom., 17, 1011-1014.
- Hou, X., Roos, P., 2008. Critical comparison of radiometric and mass spectrometric methods for the determination of radionuclides in environmental, biological and nuclear waste samples. Anal. Chim. Acta 608, 105-139.
- Hu, Q., Rose, T. P., Zavarin, M., Smith, D. K., Moran, J. E., Zhao, P., 2008. Assessing Field-Scale Migration of Radionuclides at the Nevada Test Site: "mobile" species. J. Environ. Radioactiv., 99, 1617.
- Hursthouse, A. S., Baxter, M. S., McKay, K., Livens, F. R., 1992. Evaluation of methods for the assay of neptunium and other long-lived actinides in environmental matrices. J. Radioanal. Nucl. Chem., 157 (2) 281-294.
- IAEA, 1998. The Radiological Situation at the Atolls of Mururoa and Fangataufa. STI/PUB/1028, Technical Report vol. 1, Vienna.
- Ivanova, S. A., Mikheeva, M. N., Novikov, A. P. 1994. Preconcentration of neptunium by supported liquid membranes for luminescent analysis of environmental samples. J. Radioanal. Nucl. Chem. 186 (4) 341-352.
- Kalmykov, St. N., Aliev, R. A., Sapozhnikov, D. Yu., Sapozhnikov, Yu. A., Afinogenov, A. M. 2004. Determination of Np-237 by radiochemical neutron activation analysis combined with extraction chromatography. Applied Radiation and Isotopes, Volume 60, Issues 2-4, Pages 595-599
- Keith-Roach M. J., Day J. P., Fifield L. K., Livens F.R. 2001. Measurement of  $^{237}\text{Np}$  in environmental water samples by accelerator mass spectrometry. Analyst 126(1), 58-61.
- Kenna, T. C. 2009. Using sequential extraction techniques to assess the partitioning of plutonium and neptunium-237 from multiple sources in sediments from the Ob river (Siberia). L. Environ. Radioactivity 100, 547-557
- Kenna, T. C., Sayles, F. L., 2002. The distribution and history of nuclear weapons related contamination in sediments from the Ob river, Siberia as determined by isotopic ratios of plutonium and neptunium. J. Environ. Rad. 60, 105-137.
- Ketterer, M. E., Szechenyi, S. C., 2008. Determination of plutonium and other transuranic elements by inductively coupled plasma mass spectrometry: A historical perspective and new frontiers in the environmental sciences. Spectrochimica Acta Part B: Atomic Spectroscopy, Volume 63, Issue 7, July 2008, Pages 719-737
- Kuczewski, B., Marquardt, C. M., Seibert, A., Geckeis, H., Kratz, J. V., Trautmann, N. 2003. Separation of plutonium and neptunium species by capillary electrophoresis-inductively

- coupled plasma-mass spectrometry and application to natural groundwater samples. *Anal. Chem.* 75, 6769-6774
- Lariviere, D., Taylor, V. F., Evans, R. D., Cornett, R. J., 2006. Radionuclide determination in environmental samples by inductively coupled plasma mass spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy*, Volume 61, Issue 8, August 2006, Pages 877-904
- Lindahl, P., Roos, P., Eriksson, M., Holm, E., 2004. Distribution of Np and Pu in Swedish lichen samples (*Cladonia stellaris*) contaminated by atmospheric fallout *Journal of Environmental Radioactivity* 73 (1) 73-85.
- Lindahl, P., Roos, P., Holm, E., Dahlgard, H., 2005. Studies of Np and Pu in the marine environment of Swedish–Danish waters and the North Atlantic Ocean. *Journal of Environmental Radioactivity* 82 (3) 285-301
- Ménard, O., Advocat, T., Ambrosi, J.P., Michard, A., 1998. Behaviour of actinides (Th, U, Np and Pu) and rare earths (La, Ce and Nd) during aqueous leaching of a nuclear glass under geological disposal conditions. *Applied Geochemistry*, Volume 13, Issue 1, Pages 105-126
- Myasoedov, B. F., Lebedev, I.A., 1991. Latest achievements in the analytical chemistry of actinides. *J. Radioanal. Nucl. Chem.* 147 (1), 5-26.
- Nimz, G., Thompson, J. 1992. Underground Radionuclide Migration at the Nevada Test Site. UCRL-ID-111013 LLNL report.
- Novikov, A. P., Lavrinovich, E. A., Mogilevskii, A. N., Fabelinskii, Yu. I. 2009. Luminescence analysis of underground waters of the lake Karachai contamination area for the neptunium content and forms of occurrence. *Radiochem.* 51 (5) 537-541.
- Pawloski, G.A., Tompson, A.F.B., Carle, S.F., 2001. Evaluation of the hydrologic source term from underground nuclear tests on Pahute Mesa at the Nevada Test Site: The CHESHIRE test, UCRL-ID-147023, Lawrence Livermore National Laboratory, Livermore, CA.
- Prosser, S. L., Popplewell, D. S., Lloyd, N. C. 1994. *J. Environ. Rad.* 23, 123-133.
- Röllin, S., Sahli, H., Holzer, R., Astner, M., Burger, M., 2009. Pu and Np analysis of soil and sediment samples with ICP-MS. *Applied Radiation and Isotopes* 67 (5), 821-827.
- Rosner, G., Winkler, R., Yamamoto, M. 1993. Simultaneous radiochemical determination of  $^{237}\text{Np}$  and  $^{239}\text{Np}$  with  $^{235}\text{Np}$  as tracer, and application to environmental samples. *J. Radioanal. Nucl. Chem.* 173 (2), 273-281
- Smith, D. K. Finnegan, D. L., Bowen, S. M. 2003. An Inventory of Long-Lived Radionuclides Residual From Underground Nuclear Testing at the Nevada Test Site, 1951-1992. *J. Environ. Radioactiv.*, 67, 35-51
- Truscott, J. B., Jones, P., Fairman, B. E., Evans, E. H. 2007. Determination of actinide elements at femtogram per gram levels in environmental samples by on-line solid phase extraction and sector-field-inductively coupled plasma-mass spectrometry. *Analytica Chimica Acta*, Volume 433, Issue 2, Pages 245-253
- Vajda, N., Kim, Ch.-K. 2011. Determination of transuranium (Pu, Np, Am) isotopes by

- radiometric techniques: A review of analytical methodology. *Anal. Chem.* published online April 11, 2011. Vance, D., Belt, V., Oatts, T., Mann, D. 1998. Neptunium determination by inductively coupled plasma mass spectrometry (ICP-MS). *J. Radioanal. Nucl. Chem.* 234, 143–147.
- Wang, X., Jiang, S., Dong, K., He, M., He, G., Li, C., Li, S., Gong, J., Lu, L. 2010. Development of laboratory standards for AMS measurement of Np. *Nuc. Instru. Meth. In Phys. Res. B* 268, 1949-1953.
- Yamamoto, M., Yamauchi, Y., Chatani, K., Igarashi, S., Komura, K., Ueno, K., Sakanoue, M. 1991. Distribution of global fallout  $^{237}\text{Np}$ , Pu isotopes, and  $^{241}\text{Am}$  in lake and sea sediments. *J. Radioanal. Nucl. Chem.* 147 (1), 165-176.
- Zhao, P., Hu, Q., Rose, T. P., Nimz, G. J., Zavarin, M., 2008. Distribution of  $^{99}\text{Tc}$  and  $^{129}\text{I}$  in the vicinity of underground nuclear tests at the Nevada Test Site. *J. Radioanal. Nucl. Chem.* 276 (3), 755-761.