AQUEOUS GEOCHEMISTRY OF URANIUM, LOS ALAMOS AND SURROUNDING AREAS, NEW MEXICO

Patrick Longmire, Los Alamos National Laboratory, MS D469
Los Alamos, NM 87545 plongmire@lanl.gov (505) 665-1264
Dale Counce, Los Alamos National Laboratory, MS D469
Los Alamos, NM 87545 counce@lanl.gov (505) 667-1224
Michael Dale, NMED DOE Oversight Bureau, 134 State Road 4, Suite A
White Rock, NM 87544 dale@lanl.gov (505) 672-0449

Presentation Abstract 29

This presentation provides analytical results for groundwater obtained during four characterization sampling rounds conducted at several regional aquifer and perched-intermediate wells at Los Alamos National Laboratory. Springs discharging in White Rock Canyon and in the Sierra de los Valles have also been sampled as part of this investigation. Uranium is a trace element of interest because natural background generally is less than 0.002 mg/L depending on the reactive-phase mineralogy of aquifer material, aqueous chemistry, and age and residence time of groundwater. Uranium has been processed at Los Alamos National Laboratory since the early 1940s for a variety of purposes.

Analytical results for the wells show that solute concentrations are presently below maximum contaminant levels (MCLs) established by the EPA, including uranium (MCL of 0.030 mg/L), within the regional aquifer. Groundwater collected from the regional aquifer and perched zones at Los Alamos National Laboratory is dominantly a calcium-sodium-bicarbonate type and is relatively oxidizing.

Geochemical calculations using the computer program MINTEQA2 were performed to evaluate solute speciation, mineral equilibrium, and adsorption/desorption in assessing uranium aqueous chemistry and transport. Results suggest that the regional aquifer approaches equilibrium with respect to amorphous silica phases or volcanic glass and $CaCO^3$ and is undersaturated with respect to $USiO^4$, $UO^2(OH)^2$, $MnCO^3$, and $SrCO^3$. Groundwater shows variable saturation with respect to $Ca(UO^2)^2(Si^2O^5)^3.5H^2O$ (haiweeite), based on silica activity and pH. Surface complexation modeling (diffuse layer) of U(VI) shows that ferrihydrite partly adsorbs uranyl carbonato species, which is in agreement with experimental and field observations.

Contact: Patrick Longmire, Los Alamos National Laboratory, EES-6 Group, MS D469, Los Alamos, NM 87545; plongmire@lanl.gov (505) 665-1264, fax: (505) 665-0246

Aqueous Geochemistry of Uranium, Los Alamos and Surrounding Areas, New Mexico

By

Patrick Longmire[1], Dale Counce[1], Michael Dale[2], and Kim Granzow[2]

1. **Los Alamos National Laboratory, MS D469, Los Alamos, NM 87545**
2. **NMED DOE Oversight Bureau, 134 State Road 4, Suite A, White Rock, NM 87544**

PURPOSE

Provide an overview of uranium distributions in perched intermediate groundwater and in the regional aquifer.

Discuss results of geochemical modeling focusing on uranium speciation, mineral equilibria, and adsorption reactions.

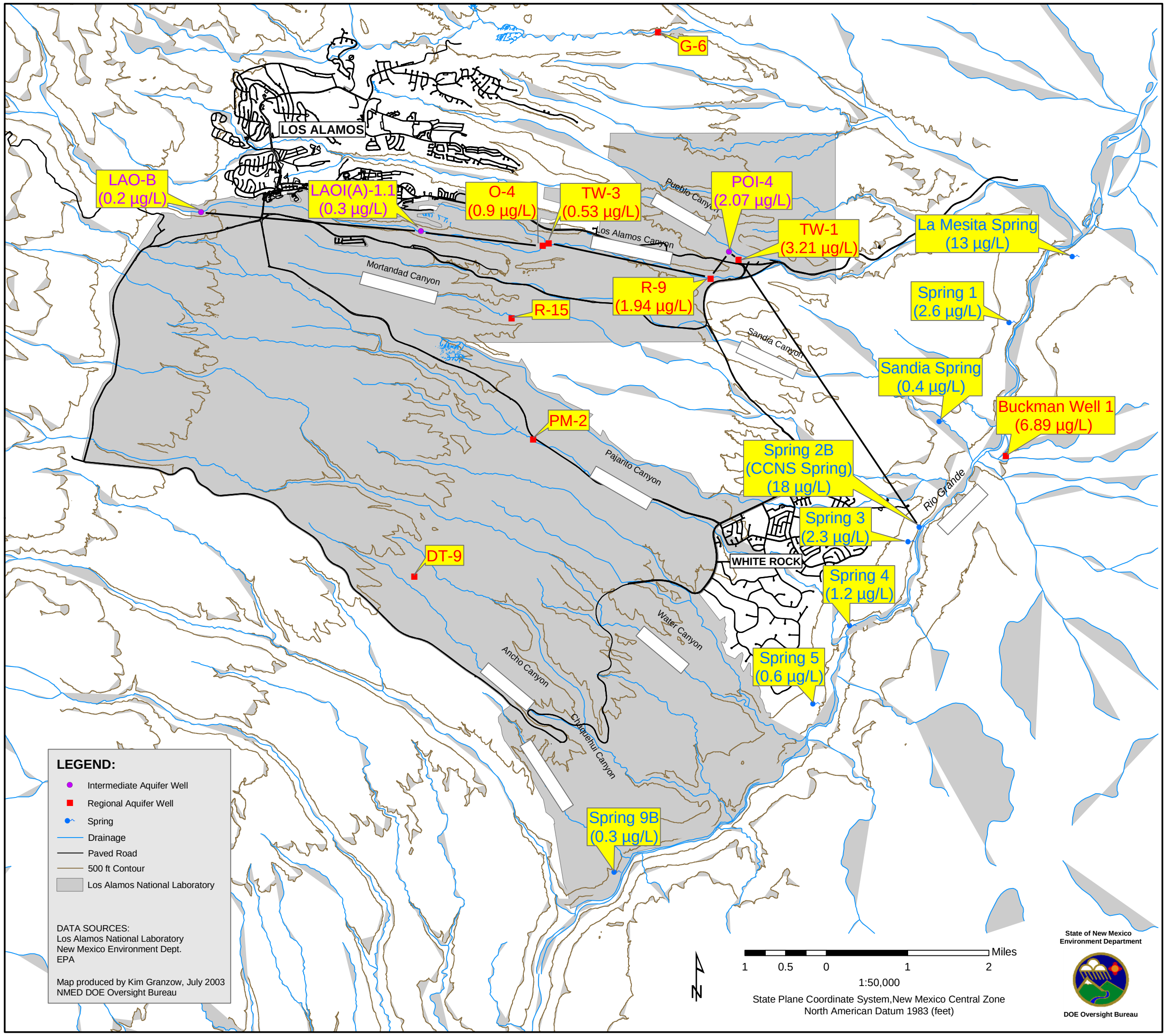
ANALYTICAL METHODS

Inductively coupled plasma optical emission spectroscopy (ICPOES)
Al, Ca, Fe, Mg, Mn, Na, K, and Si

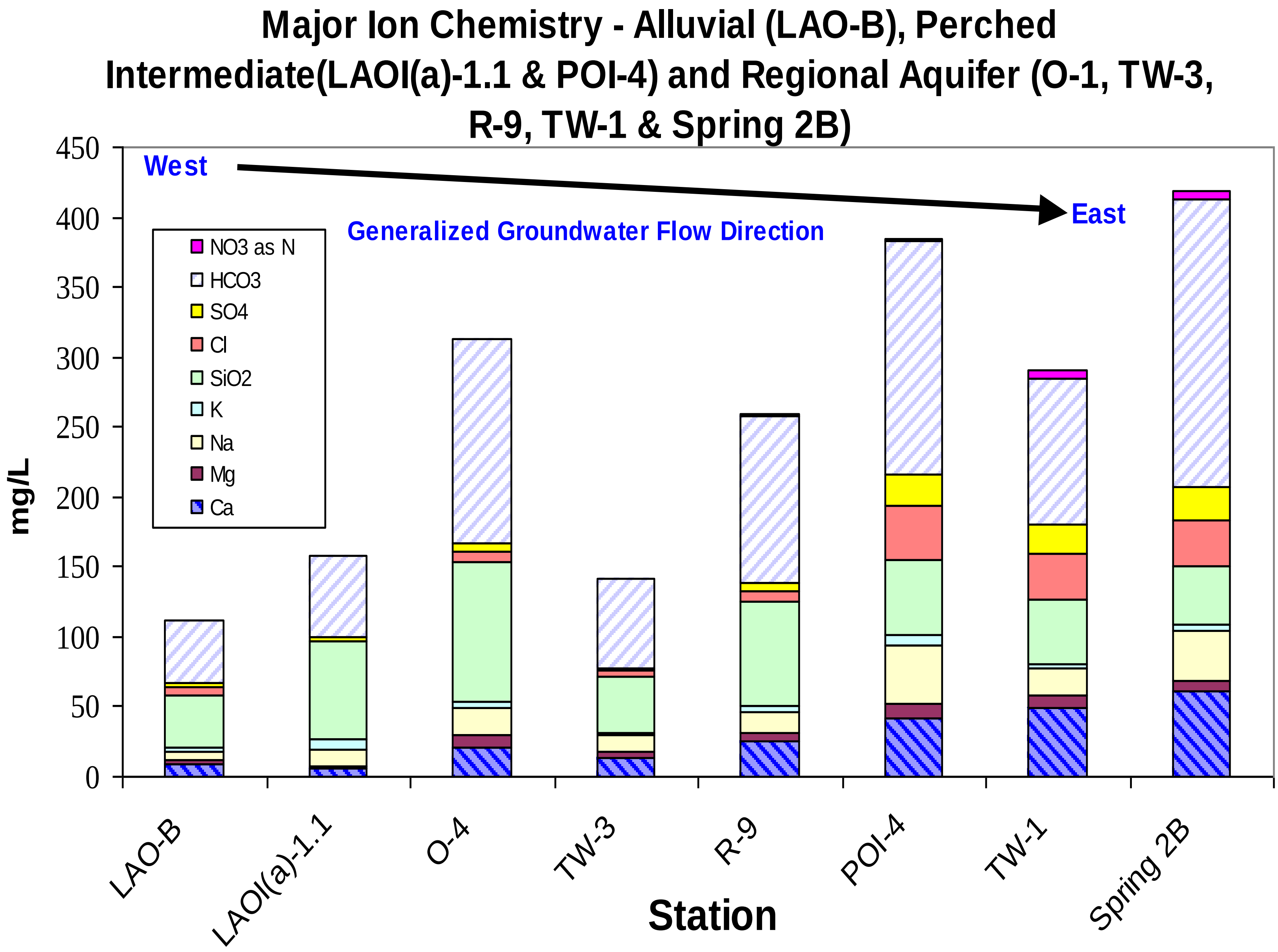
Inductively coupled plasma mass spectrometry (ICPMS)
Sb, As, B, Ba, Be, Cd, Co, Cr, Cu, Mo, Ni, Pb, Se, Sr, Th, Tl, U, V, and Zn

Ion Chromatography
Cl, Br, F, NO_3, NO_2, PO_4, and SO_4

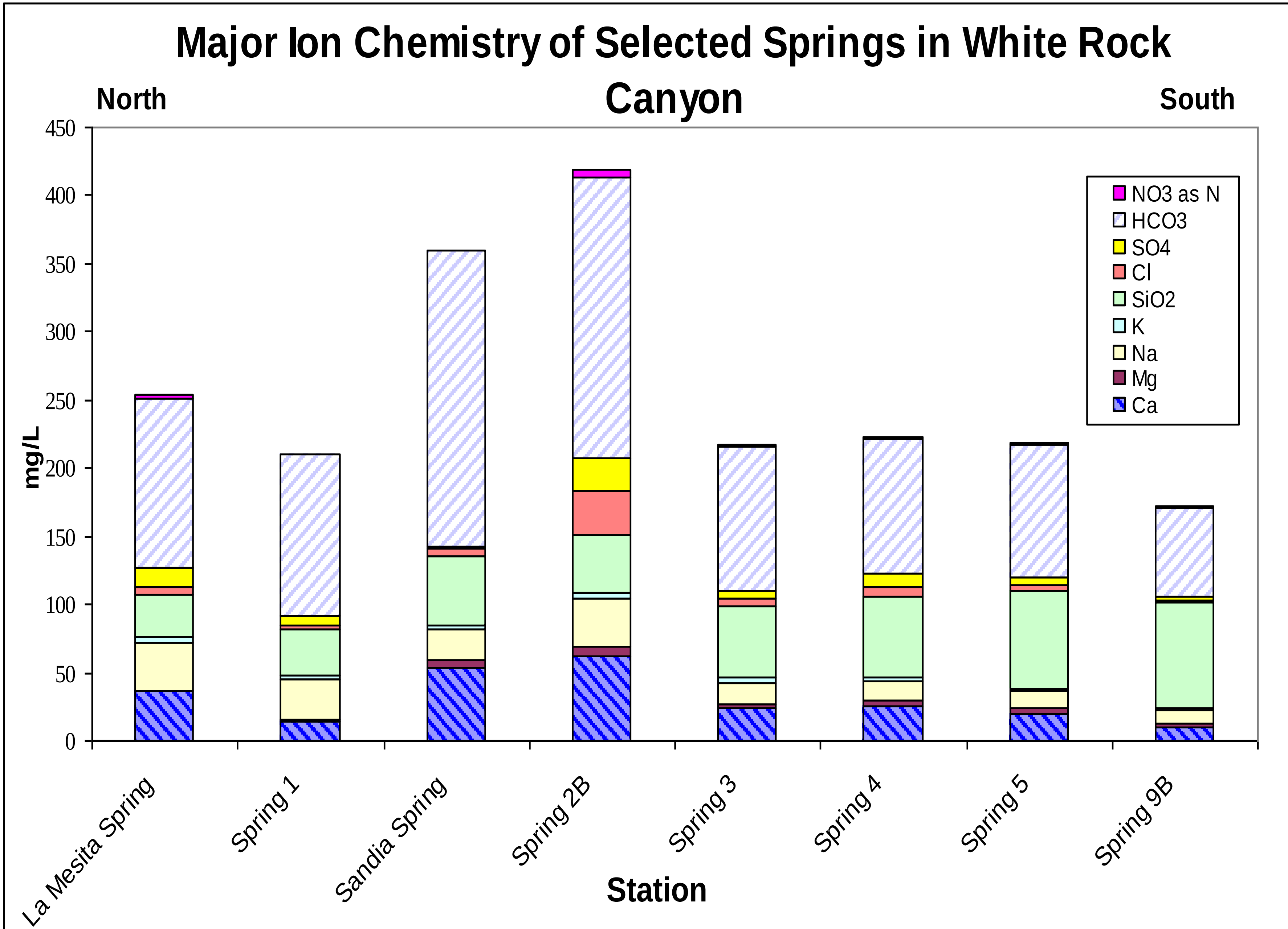
Alkalinity: Titration



Ground-Water Stations and Associated Uranium Concentrations (µg/L) from 1999-2002
Filtered and Non-filtered Samples



Major Ion Chemistry - Alluvial (LAO-B), Perched Intermediate(LAOI(a)-1.1 & POI-4) and Regional Aquifer (O-1, TW-3, R-9, TW-1 & Spring 2B)
West
East
Generalized Groundwater Flow Direction
NO3 as N
HCO3
SO4
Cl
SiO2
K
Na
Mg
Ca
mg/L
450
400
350
300
250
200
150
100
50
0
LAO-B
LAOI(a)-1.1
O-4
TW-3
R-9
POI-4
TW-1
Spring 2B
Station



Major Ion Chemistry of Selected Springs in White Rock Canyon
North
South
mg/L
0
50
100
150
200
250
300
350
400
450
NO3 as N
HCO3
SO4
Cl
SiO2
K
Na
Mg
Ca
La Mesita Spring
Spring 1
Sandia Spring
Spring 2B
Spring 3
Spring 4
Spring 5
Spring 9B
Station

SOURCES OF URANIUM

<u>Natural</u> – Uranium is present in trace phases within the Bandelier Tuff, Puye Formation, and Cerros del Rio basalt. Whole rock concentrations of uranium range from < 1 mg/kg to > 10 mg/kg in these hydrogeologic units.

Uranium-bearing solid phases, at pH 7, have varying solubility in which silica glass ($10^{-2.71}$ M) is the most soluble and zircon ($10^{-15.54}$ M) is the least soluble.

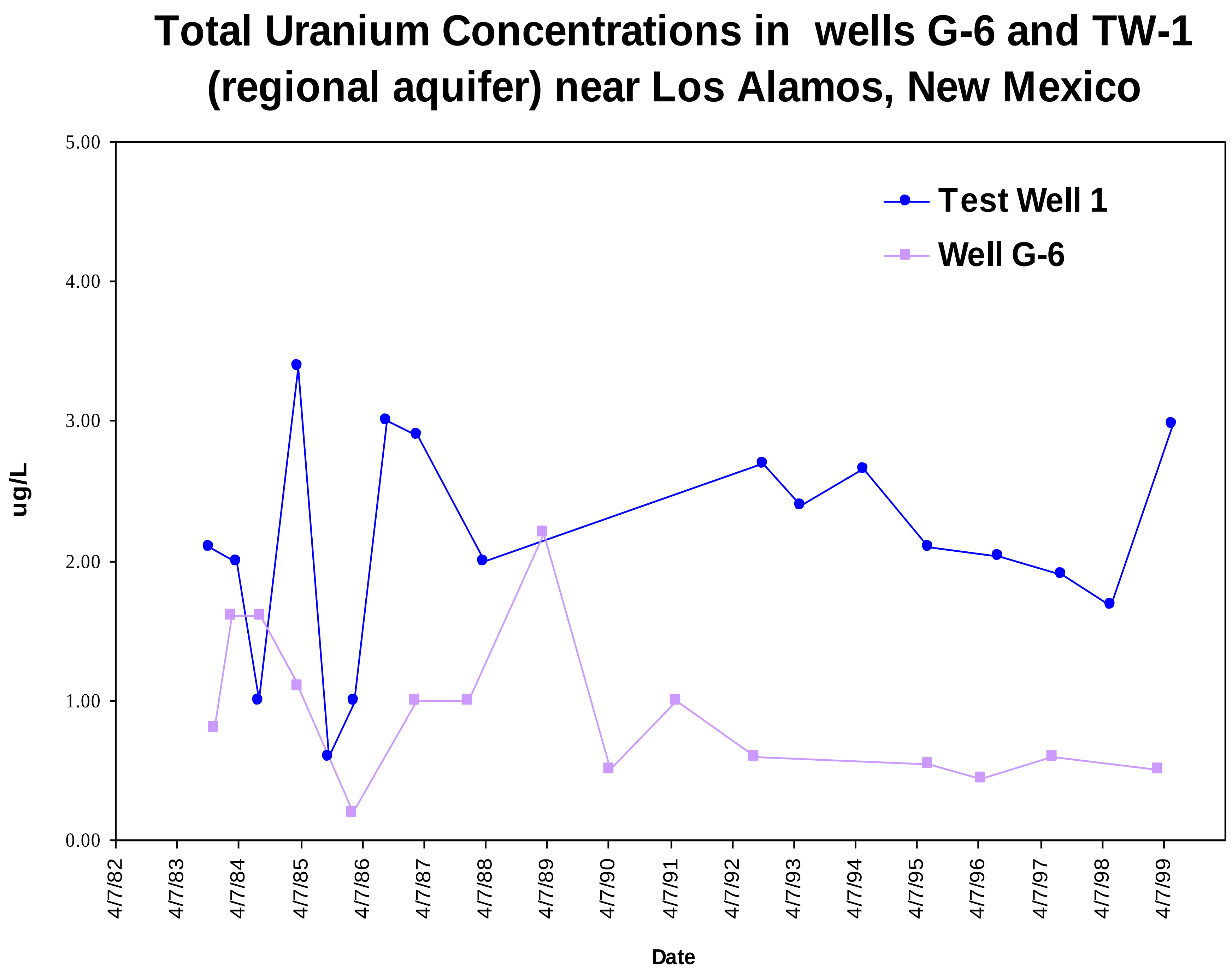
Dissolved concentrations of uranium in perched zones and in the regional aquifer beneath the Pajarito Plateau are typically less than 2 μg/L.

<u>Laboratory</u> – Uranium is used at Los Alamos for research and defense purposes, including enriched, natural, and depleted uranium. Solid and aqueous forms of uranium have been released to the environment.

Statistical Distribution of Uranium in Groundwater from the Pajarito Plateau and Surrounding Areas

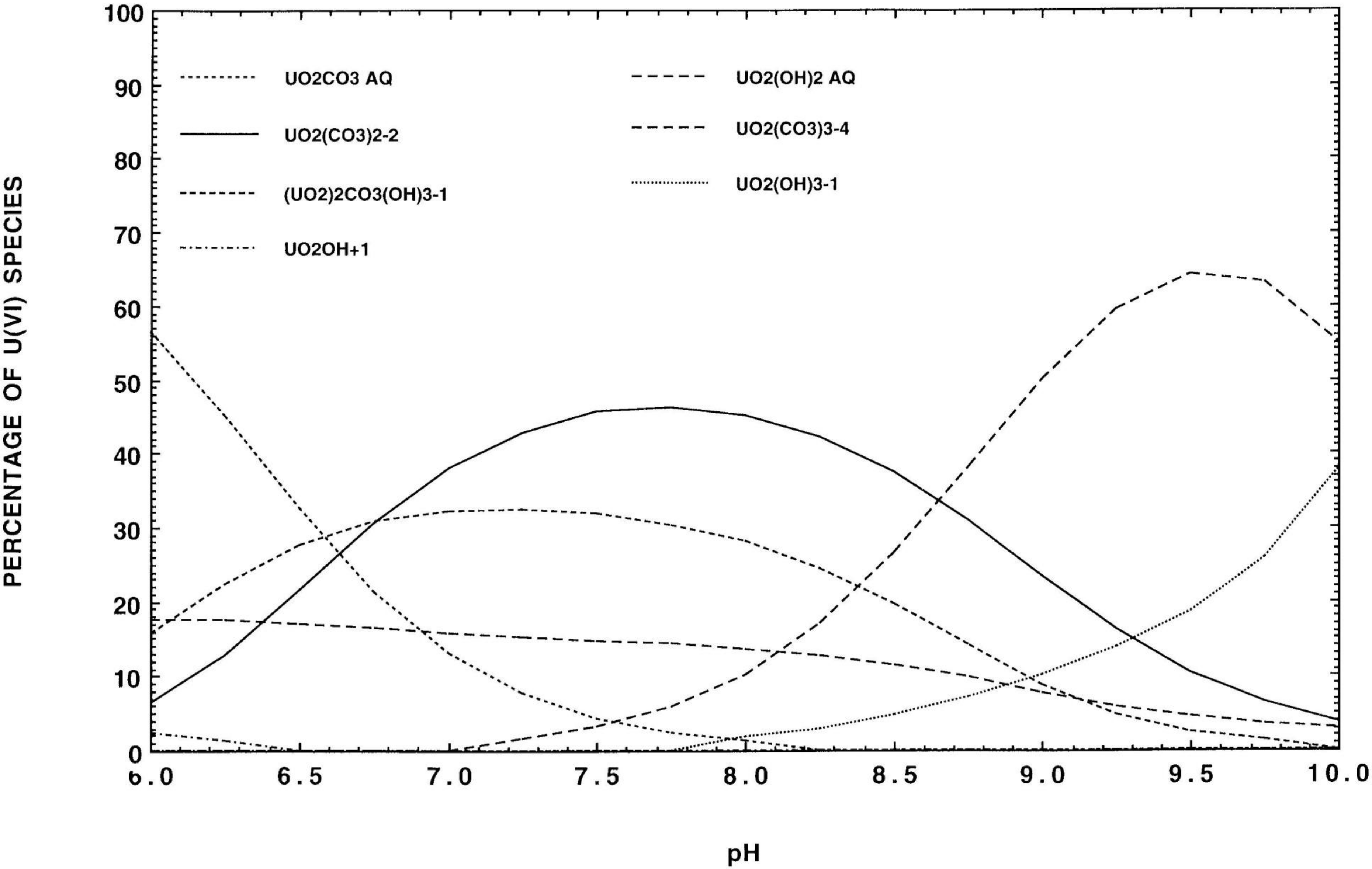
Statistic	Value (μg/L)
Number of samples	65
Mean	1.86
Standard error	0.47
Median	0.68
Std. Dev.	3.78
Kurtosis	14.15
Skew	3.69
Min	0.05
Max	19.64 (La Mesita Spring)

Source: Environmental Surveillance and Compliance Programs, 1997



Total Uranium Concentrations in wells G-6 and TW-1
(regional aquifer) near Los Alamos, New Mexico
Test Well 1
Well G-6
ug/L
5.00
4.00
3.00
2.00
1.00
0.00
4/7/82
4/7/83
4/7/84
4/7/85
4/7/86
4/7/87
4/7/88
4/7/89
4/7/90
4/7/91
4/7/92
4/7/93
4/7/94
4/7/95
4/7/96
4/7/97
4/7/98
4/7/99
Date

FIGURE 5. RESULTS OF SPECIATION CALCULATIONS FOR WATER CANYON GALLERY WATER USING MINTEQA2, LOS ALAMOS, NEW MEXICO. LOG U(VI) = -5.44 M AND LOG CO3-2 = -3.07 M AT 25C.



Summary of Statistical Parameters for Distribution Coefficients (Kd) (mL/g) for the Bandelier Tuff using Water Canyon Gallery Groundwater, Los Alamos National Laboratory, Los Alamos, New Mexico

Statistic	Uranium
Mean	5.14
Median	4.85
Std. Dev.	2.98
Skew	0.10
Min	1.33
Max	9.19
Sample number	12

The pH of Water Canyon Gallery groundwater after sorption = 7.3 at 25 C. Sample depth intervals for the Bandelier Tuff are 65.0-66.0 ft, 74.0-75.0 ft, 79.1-79.7 ft, 79.9-80.0 ft, 91.0-91.5 ft, and 108.5-109.0 ft BGS. Two rock samples from each depth interval were used in the adsorption experiments. Source: Longmire et al. 1996.

INSERT NEW SATURATION INDEX PLOT-PAT WILL PROVIDE (DELETE OLD SATURATION INDEX PLOT)

Surface Complexation of Uranium (VI) Species

$UO2(CO_3)_3^{4-}$

OH^0.... UO_2^{2+}

Site 1 (strong)

$UO_2(CO_3)_2^{2-}$

O^-.... UO_2^{2+}

Site 2 (weak)

$Fe(OH)_3$

HFO

"hydrous ferric oxide"

$UO_2CO_3^0$

SURFACE COMPLEXATION MODELING OF LANL WELL R-9 GROUND WATER: DIFFUSE LAYER MODEL

The diffuse-layer adsorption model considers solution speciation and aqueous ion activities. The model uses the electric double-layer (EDL) theory. EDL theory assumes that the + or – surface charge of an adsorbent in contact with solution generates an electrostatic potential that declines rapidly away from the adsorbent surface. The potential is the same at the zero (adsorbent surface) and d (solution) planes.

The concentration of hydrous ferric oxide (HFO) at 275 ft in the basalt perched zone at well R-9 is 1.46 g/L based on total iron analyses for groundwater.

SURFACE COMPLEXATION MODELING OF LANL WELL R-9 GROUND WATER: DIFFUSE LAYER MODEL

The specific surface area of HFO is 600 m2/g.

Model uranyl sorption with one surface containing two sites, high energy (s) (8.2×10^{-5} mol active site HFO/L) and low energy (w) (0.003 mol active site HFO/L). The estimated intrinsic constants for uranyl sorption (Langmuir, 1997) include:

$\equiv Fe_sOH + UO_2^{2+} = \equiv Fe_sOHUO_2^{2+}$ **(log K_1 = 5.2) and**

$\equiv Fe_wOH + UO_2^{2+} - H^+ = \equiv Fe_wOUO_2^+$ **(log K_2 = 2.8).**

-

SURFACE COMPLEXATION MODELING OF LANL WELL R-9: DIFFUSE LAYER MODEL

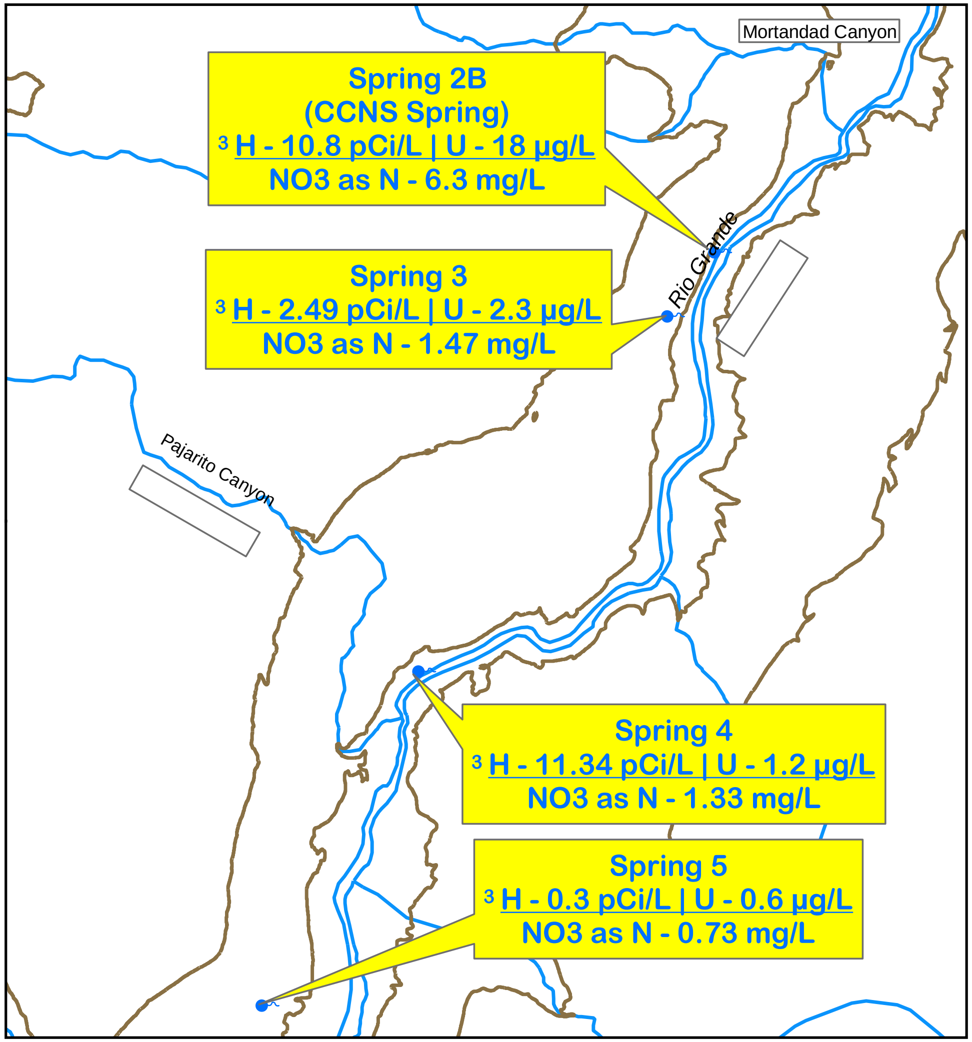
-

The DLM predicts that 112 ppb total uranium in the 275 ft basalt perched zone (LANL) at pH 9 occurs as

57.5 percent uranyl bound as SO2UO2+
(64 ppb sorbed U),

5.1 percent uranyl bound as $UO_2(CO_3)_2^{2-}$
(7 ppb dissolved U), and

36.6 percent uranyl bound as $UO_2(CO_3)_3^{4-}$ (41 ppb dissolved U) (calculated total dissolved U is 48 ppb, measured dissolved U is 48.4 ppb).



Spring
Drainage
500 ft Contour

1,000 0 1,000 2,000 Feet
1:24,000
1 inch = 2000 feet

N

State of New Mexico
Environment Department

DATA SOURCES:
Los Alamos National Laboratory
New Mexico Environment Dept.
EPA

PROJECTION:
New Mexico State Plane Coordinate System
Central Zone
North American Datum, 1983, Feet

Map produced by Kim Granzow, July 2003
NMED DOE Oversight Bureau

White Rock Canyon Springs Between Mortandad and Water Canyons

DOE Oversight Bureau

SURFACE COMPLEXATION MODELING OF URANIUM ADSORPTION OF SPRING 2B: DIFFUSE LAYER MODEL

-

The concentration of hydrous ferric oxide (HFO) is estimated at 0.0089 g/L based on total iron anaysis.

The specific surface area of HFO is 600 m^2/g.

The DLM predicts that 24 ppb total uranium (as UO_2^{2+}) at Spring 2B (CCNS) at pH 7.58 occurs as

2.6 percent uranyl bound as ≡SO2UO2+
(0.6 ppb sorbed U),

47.9 percent uranyl bound as UO2(CO3)22-
(11.5 ppb dissolved U), and

SURFACE COMPLEXATION MODELING OF URANIUM ADSORPTION OF SPRING 2B: DIFFUSE LAYER MODEL

-

49.5 percent uranyl bound as $UO_2(CO_3)_3^{4-}$ (11.9 ppb dissolved U) (calculated total dissolved U is 23.4 ppb, measured dissolved U is 24.0 ppb).

CONCLUSIONS

Concentrations of uranium are typically less than 2 μg/L beneath the Pajarito Plateau in supply (regional aquifer) and monitoring wells (regional aquifer and perched groundwater).

Uranium(VI) species are stable as uranyl carbonato complexes that are semi adsorbing onto ferrihydrite.

Uranium concentrations above 2 μg/L occur at selected springs (La Mesita and 2B) and in Los Alamos Canyon, Mortandad Canyon, and Pueblo Canyon.

Dissolved uranium at spring 2B is characterized by a natural isotopic ratio of $^{238}U/^{235}U$ equal to 137.83 ± 0.06 (2σ). The source of uranium at this spring remains unknown.