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

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ABSTRACT

This presentation provides analytical results for groundwater obtained during several sampling rounds conducted at regional aquifer and perched-intermediate wells drilled at Los Alamos National Laboratory (LANL). Springs discharging in White Rock Canyon and in the Sierra de los Valles have also been sampled as part of this investigation. Several wells near the Rio Grande were also sampled and analyzed. Uranium is a trace element of interest because the natural background generally is less than 2 μg/L depending on the reactive-phase mineralogy of aquifer material, aqueous chemistry, and age and residence time of groundwater. Uranium has been processed at LANL since the early 1940s for a variety of purposes. Arsenic is another trace element of interest with natural background typically ranging between 3 and 20 μg/L depending on pH and total dissolved solids. Natural arsenic is associated with ferrihydrite, smectite, manganese (oxy)hydroxide, and calcium carbonate (calcite), which occur as trace phases within the regional aquifer.

Analytical results show that uranium concentrations in groundwater are presently below the EPA maximum contaminant level of 0.030 mg/L. Concentrations of arsenic in groundwater are also below the current EPA maximum contaminant level of 0.050 mg/L. Concentrations of natural arsenic and uranium within the regional aquifer increase east of the Pajarito Plateau near the Rio Grande. Groundwater within the regional aquifer and perched intermediate zones at LANL is dominantly a calcium-sodium-bicarbonate type and is relatively oxidizing. These conditions enhance the stability of aqueous uranium(VI) and arsenic(V) species and influence their fate and transport within the saturated zone.

Geochemical calculations using the computer program MINTEQA2 were performed to evaluate solute speciation, mineral equilibrium, and adsorption processes in assessing arsenic and uranium chemistry and transport. Results suggest that groundwater within the regional aquifer approaches equilibrium with respect to amorphous silica phases or volcanic glass and $CaCO_3$. This groundwater is undersaturated with respect to $(UO_2)_2SiO_4 \cdot 2H_2O$ (soddyite), $UO_2(OH)_2$, and $SrCO_3$. Regional aquifer groundwater shows variable saturation with respect to $Ca(UO_2)_2(Si_2O_5)_3 \cdot 5H_2O$ (haiweeite), based on silica and uranyl activities and pH. Surface complexation (diffuse layer model) of U(VI) shows that ferrihydrite partly adsorbs uranyl carbonate species, which is in agreement with experimental and field observations. Other natural adsorbents present in the regional aquifer include smectite, manganese (oxy)hydroxides, zeolites, and calcium carbonate (calcite).

Arsenic(III and V) species are stable in groundwater as oxyanions and are calculated not to be in equilibrium with arsenic-bearing solids. Adsorption processes most likely control transport of natural arsenic within the regional aquifer. Adsorption of arsenic onto ferrihydrite was evaluated using the diffuse layer model contained in MINTEQA2. Arsenate and arsenite species tend to desorb from ferrihydrite under basic pH conditions characteristic of the regional aquifer near the Rio Grande. Based on MINTEQA2 simulations, both bicarbonate and sulfate can compete for adsorption sites resulting in desorption and elevated concentrations of natural arsenic.

PURPOSE

Provide an overview of uranium and arsenic distributions in groundwater.

Discuss results of geochemical modeling focusing on uranium speciation, mineral equilibrium, 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, Mn, 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

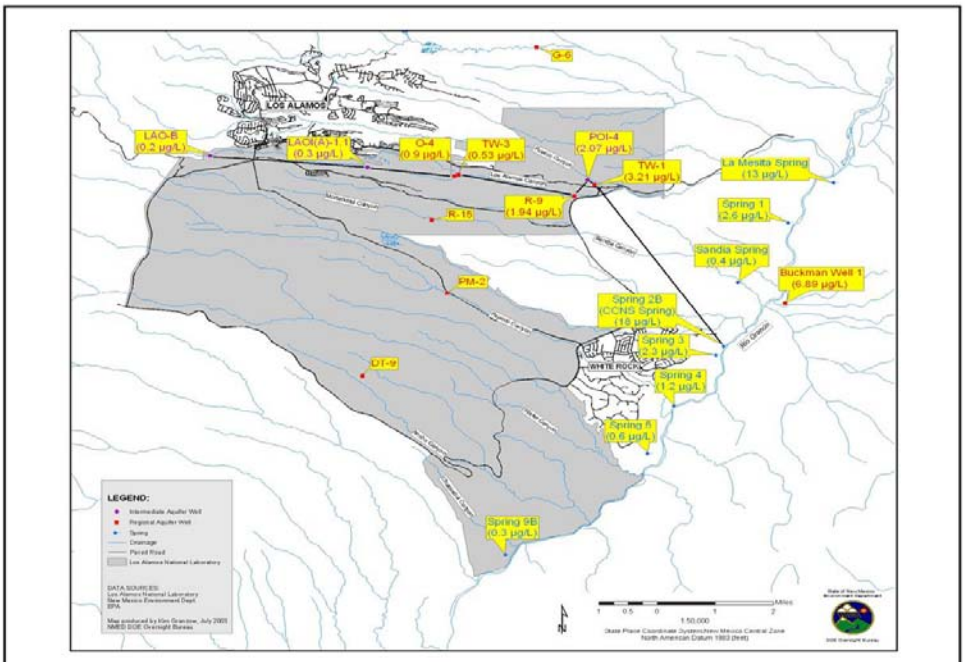
SOURCES OF URANIUM

Natural **– 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.**

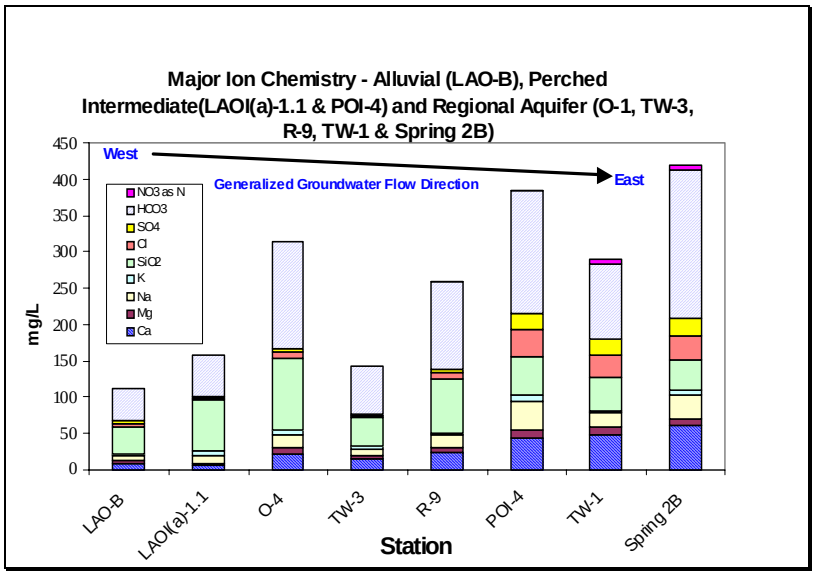
Uranium-bearing solid phases, at pH 7, have varying solubility in which silica glass ($10^{-2.71}$ M) is the most soluble and zircon ($10^{-15.54}$ M) is the least soluble.

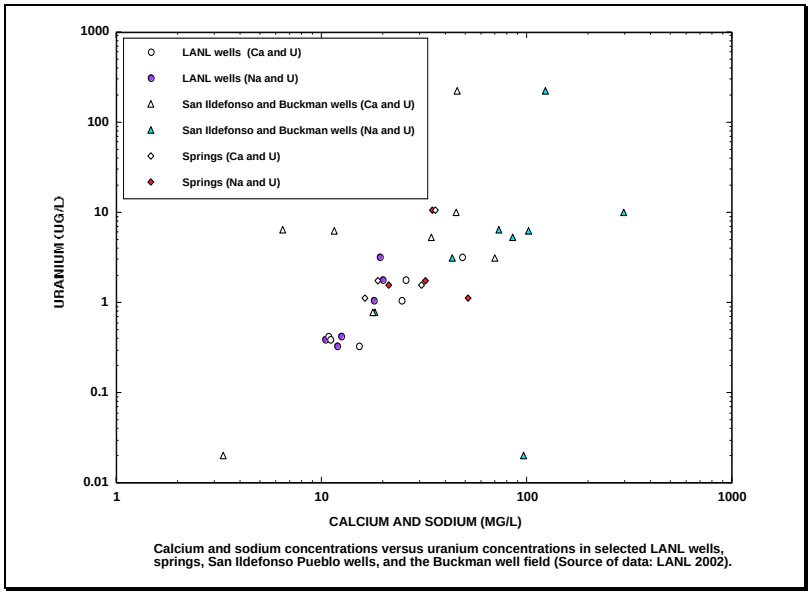
Dissolved concentrations of uranium in perched zones and in the regional aquifer beneath the Pajarito Plateau are typically less than 2 µg/L.

Laboratory **– 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.**

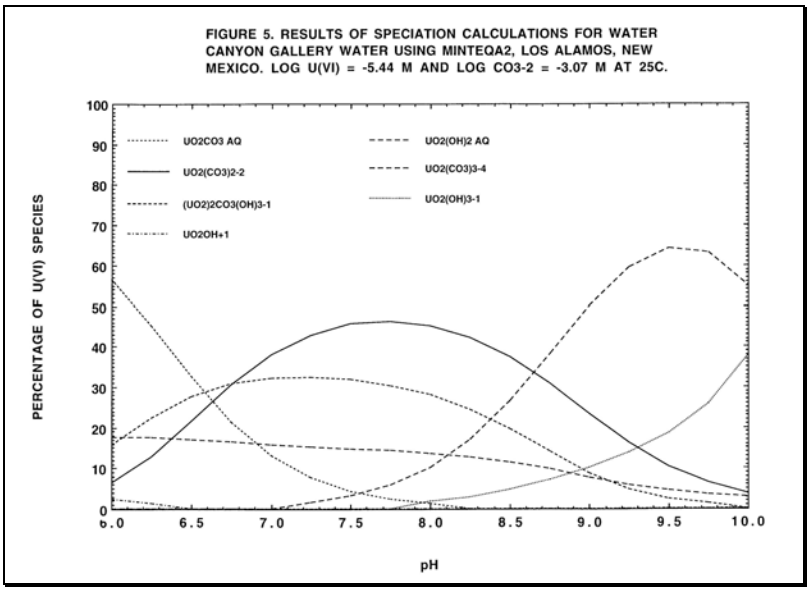


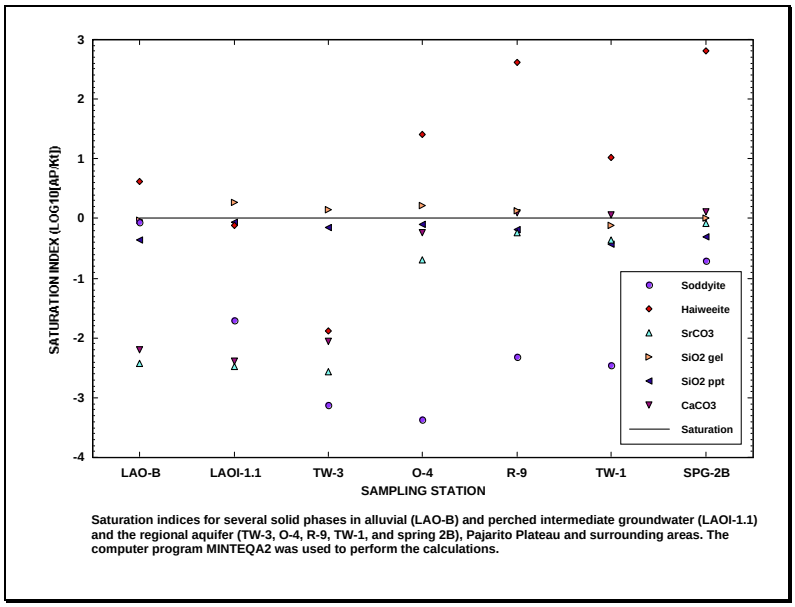
Ground-Water Stations and Associated Uranium Concentrations (µg/L) from 1999-2002 Filtered and Non-filtered Samples



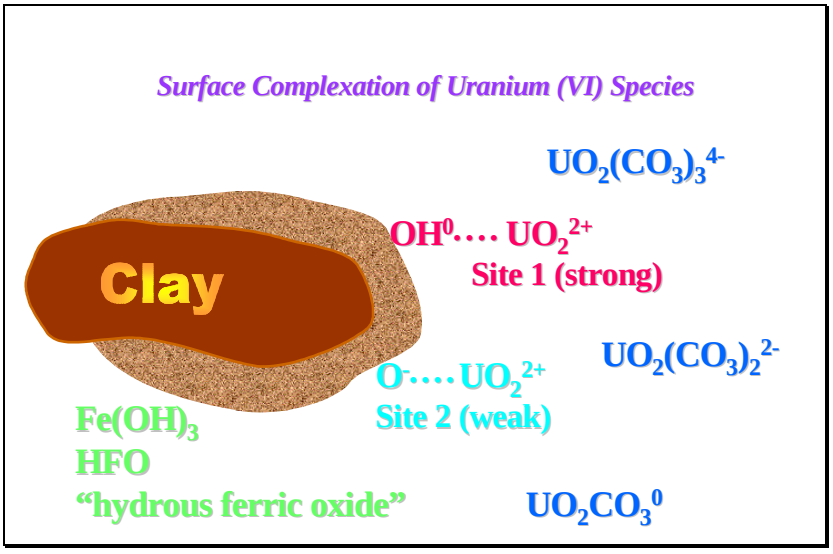


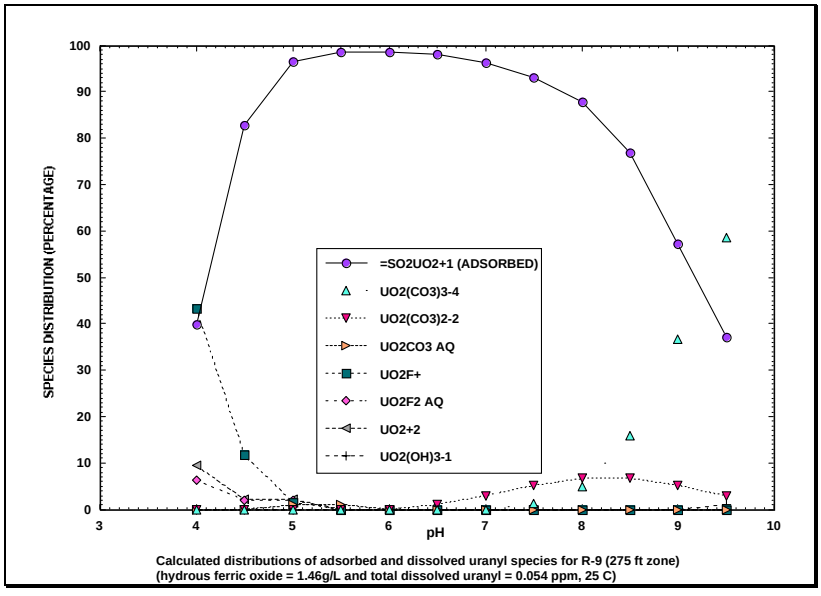
Calcium and sodium concentrations versus uranium concentrations in selected LANL wells, springs, San Ildefonso Pueblo wells, and the Buckman well field (Source of data: LANL 2002).





Saturation indices for several solid phases in alluvial (LAO-B) and perched intermediate groundwater (LAOI-1.1) and the regional aquifer (TW-3, O-4, R-9, TW-1, and spring 2B), Pajarito Plateau and surrounding areas. The computer program MINTEQA2 was used to perform the calculations.





Calculated distributions of adsorbed and dissolved uranyl species for R-9 (275 ft zone) (hydrous ferric oxide = 1.46g/L and total dissolved uranyl = 0.054 ppm, 25 C)

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 analysis.

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 adsorbed as ≡SO2UO_2^{+} (0.6 ppb U),

47.9 percent uranyl dissolved as $UO_2(CO_3)_2^{2-}$ (11.5 ppb U),

and 49.5 percent uranyl dissolved as $UO_2(CO_3)_3^{4-}$ (11.9 ppb U).

Calculated total dissolved U (as UO_2^{2+}) is 23.4 ppb, measured total U is 24.0 ppb.

OXIDATION AND REDUCTION CHEMISTRY OF ARSENIC

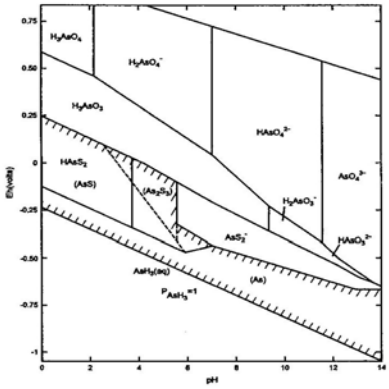


Figure 1. The Eh-pH diagram for As at 25°C and one atmosphere with total arsenic 10^{-5} mol l^{-1} and total sulfur 10^{-3} mol l^{-1}. Solid species are enclosed in parentheses in cross-hatched area, which indicates solubility less than $10^{-5.3}$ mol l^{-1}. Reprinted from Ferguson and Gavis (1972) with permission from Elsevier Science.

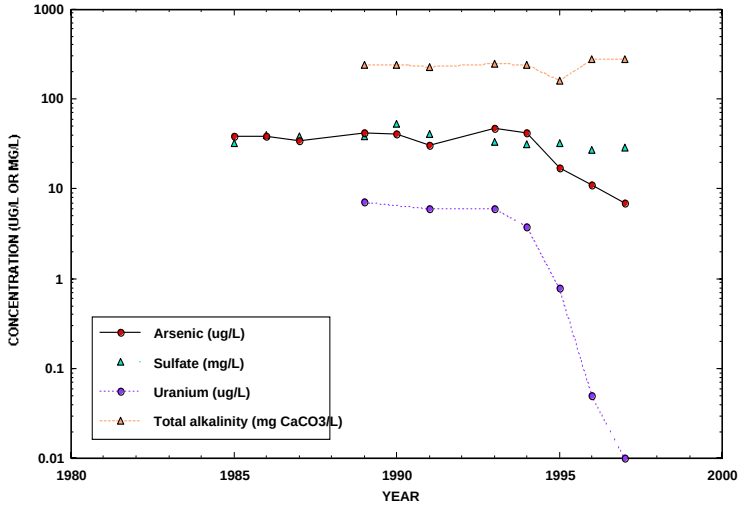


Figure 5. Time versus concentrations of arsenic (ug/L), sulfate (mg/L), uranium (ug/L), and total alkalinity (mgCaCO3/L) for well LA-1B, lower Los Alamos Canyon.

ARSENIC (III, V) ADSORPTION ONTO FERRIHYDRITE

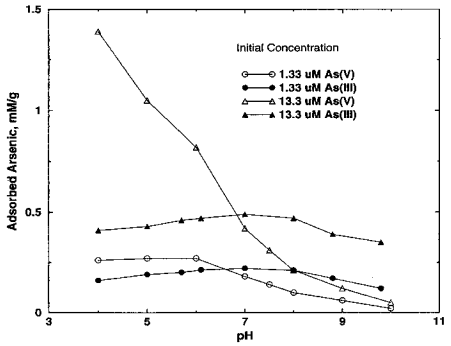


Figure 4. Adsorption of As(V) and As(III) by ferrihydrite as a function of pH. Ionic strength, 0.01 M; concentration of ferrihydrite, 0.00445 g/L. (Modified from Pierce and Moore, 1982).

CONCLUSIONS

Concentrations of U and As are typically less than 2 µg/L in groundwater beneath the Pajarito Plateau.

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

Natural As concentrations above 10 µg/L occur in lower Los Alamos Canyon. Pumping of supply wells influence As concentrations.

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

Arsenic(V) is stable as $HAsO_4^{2-}$ between pH 8.0 and 9.5. Arsenic(V) desorbs from ferrihydrite with increasing pH.