# Isotope and Aqueous Chemistry Investigations of Groundwater in the Española Basin, New Mexico

(LA-UR-08-0945)

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# Motivation of Study

Establish an understanding of the groundwater flow system at Los Alamos (water sources, mixing relations, flow paths, and travel times) that is independent of numerical models.

Evaluate natural and anthropogenic sources of chromium and uranium in the subsurface.

Of particular interest is the vulnerability of natural discharge areas near the Rio Grande to contamination.

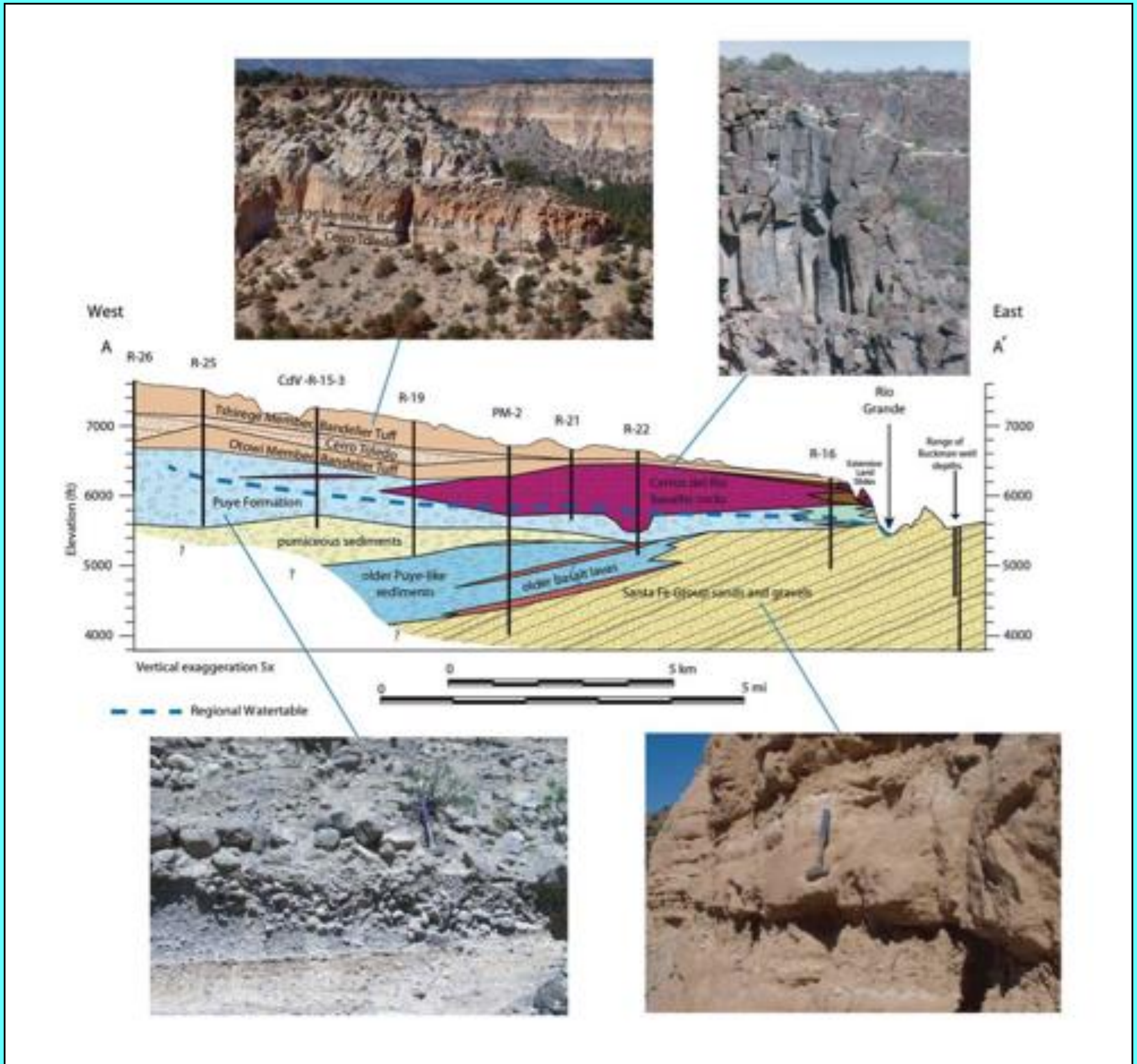
# Topics of Interest

- *Groundwater Age* (Tritium/helium-3 and carbon-14 dating methods)
- *Delineation of Groundwater Flow Paths*
- *Aqueous Chemistry of Chromium and Uranium*

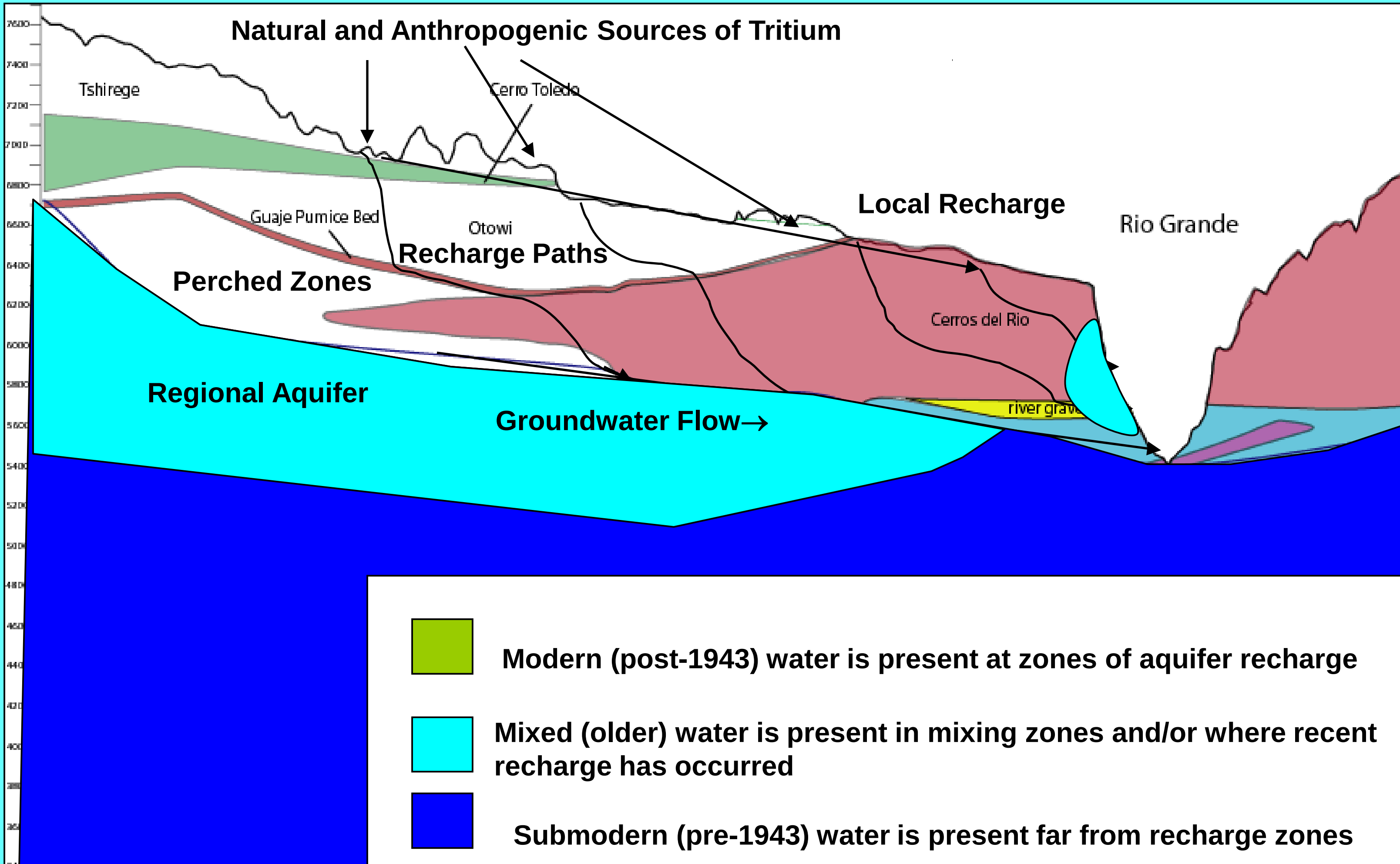
# Analytical Methods

- **Carbon-14**, accelerator mass spectrometry
- **Tritium**, helium ingrowth and electrolytic enrichment
- **Stable isotopes**, isotope ratio mass spectrometry
- **Anions**, ion chromatography
- **Metals**, inductively couple (argon) plasma-optical emission spectroscopy (ICP-OES) and inductively couple (argon) plasma-mass spectrometry (ICP-MS)
- **Total carbonate alkalinity**, titration

# LANL Stratigraphy



# Generalized Expected Trends in Groundwater Age for Conceptual Model of Groundwater Flow

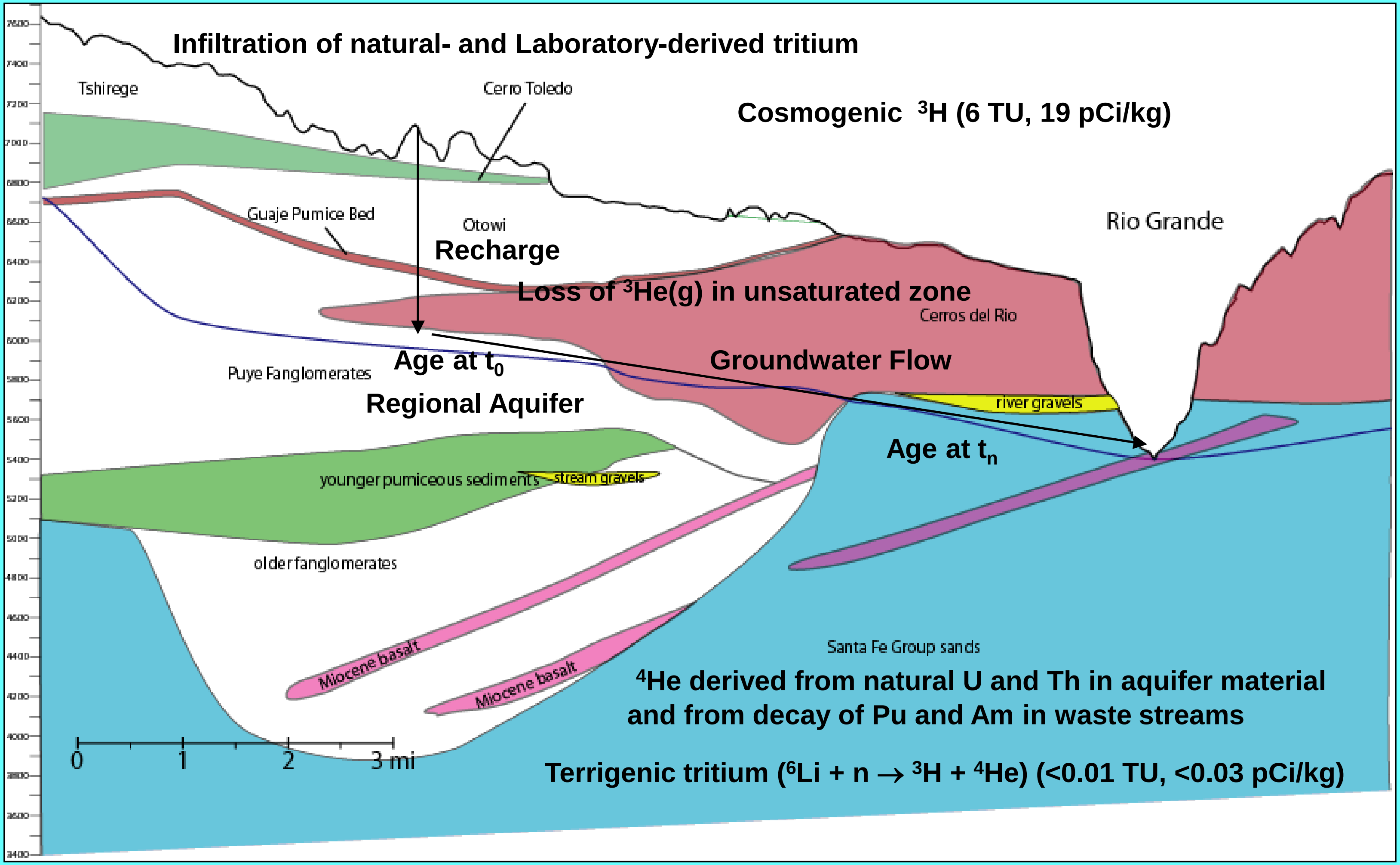



Modern (post-1943) water is present at zones of aquifer recharge

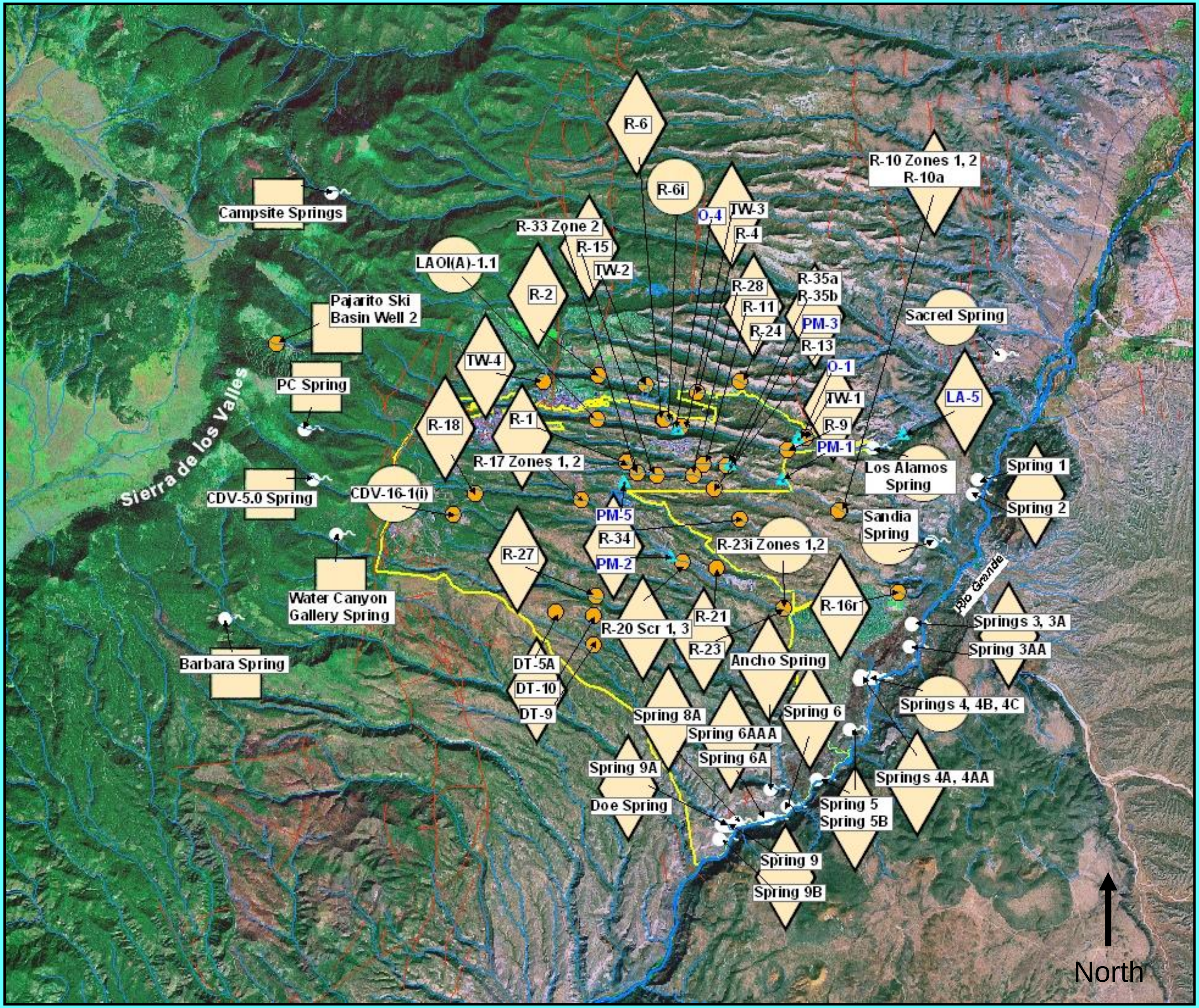
Mixed (older) water is present in mixing zones and/or where recent recharge has occurred

Submodern (pre-1943) water is present far from recharge zones

# Conceptual Model for Tritium and Helium



# Sampling Stations for Hydrochemical Investigation



# Median Background Composition of the Regional Aquifer, Los Alamos, New Mexico

| Analyte | Millimoles/Liter | Milligrams/Liter |
|---|---|---|
| Ca | 0.29 | 11.7 |
| Mg | 0.12 | 2.96 |
| Na | 0.54 | 12.50 |
| K | 0.04 | 1.89 |
| Cl | 0.06 | 2.22 |
| $SO_4$ | 0.03 | 2.90 |
| $HCO_3$ | 1.18 | 68.80 |
| F | 0.02 | 0.32 |
| $SiO_2$ | 1.16 | 69.55 |
| Cr | 5.87e-05 | 0.00305 |
| $NO_3$(N) | 0.04 | 0.54 |
| U | 1.89e-06 | 0.00045 |

# Stable Isotope Results for Springs and Wells, Pajarito Plateau, New Mexico

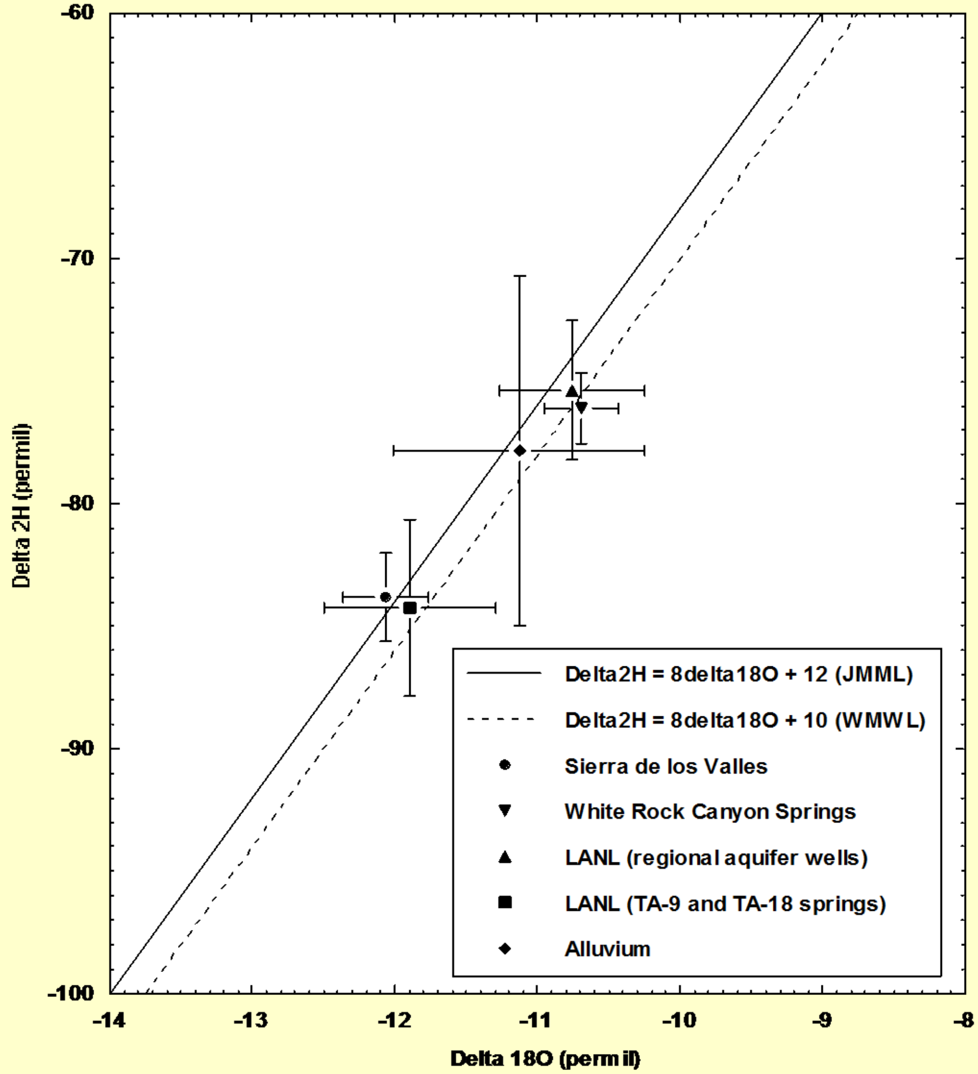
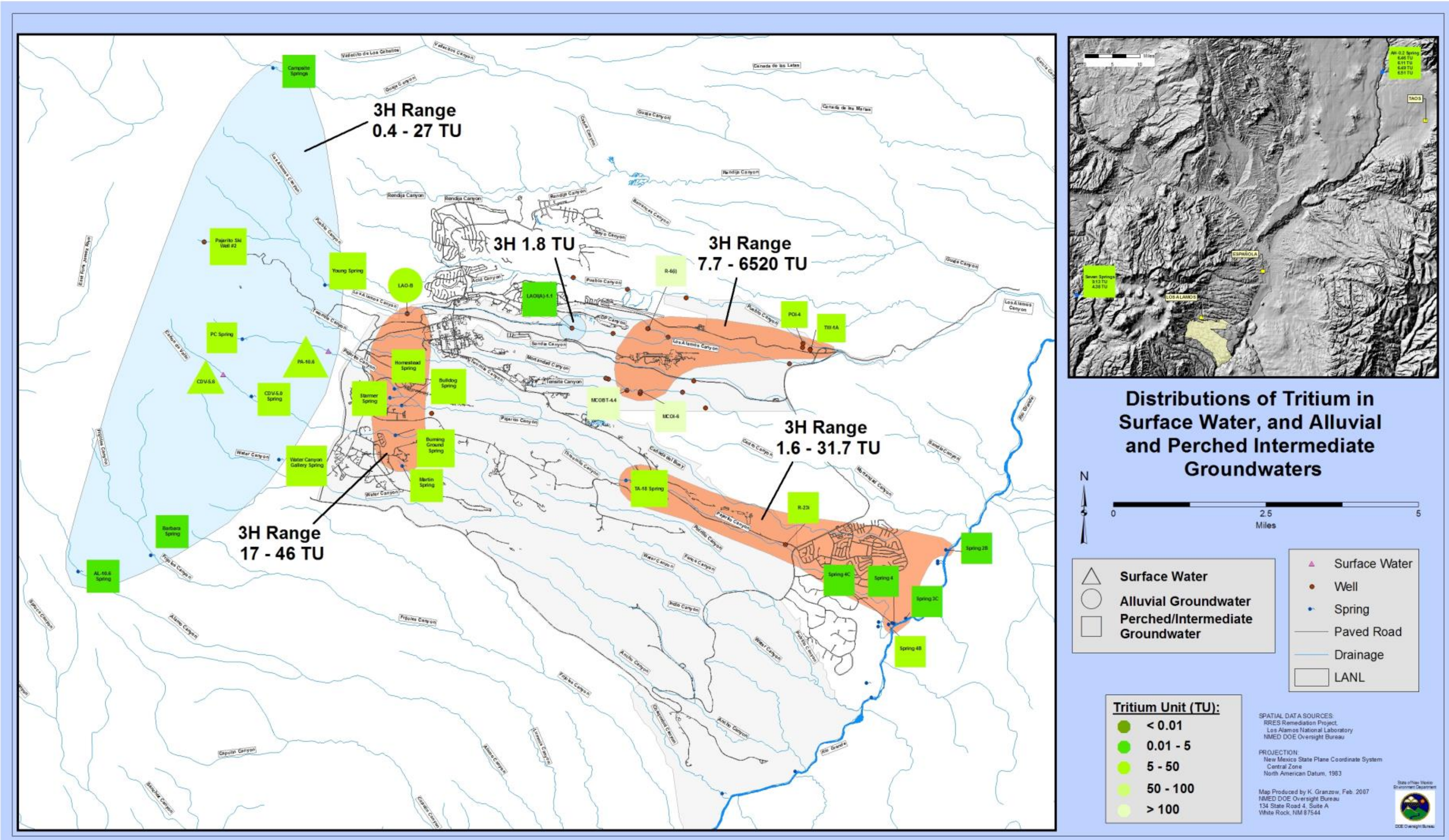
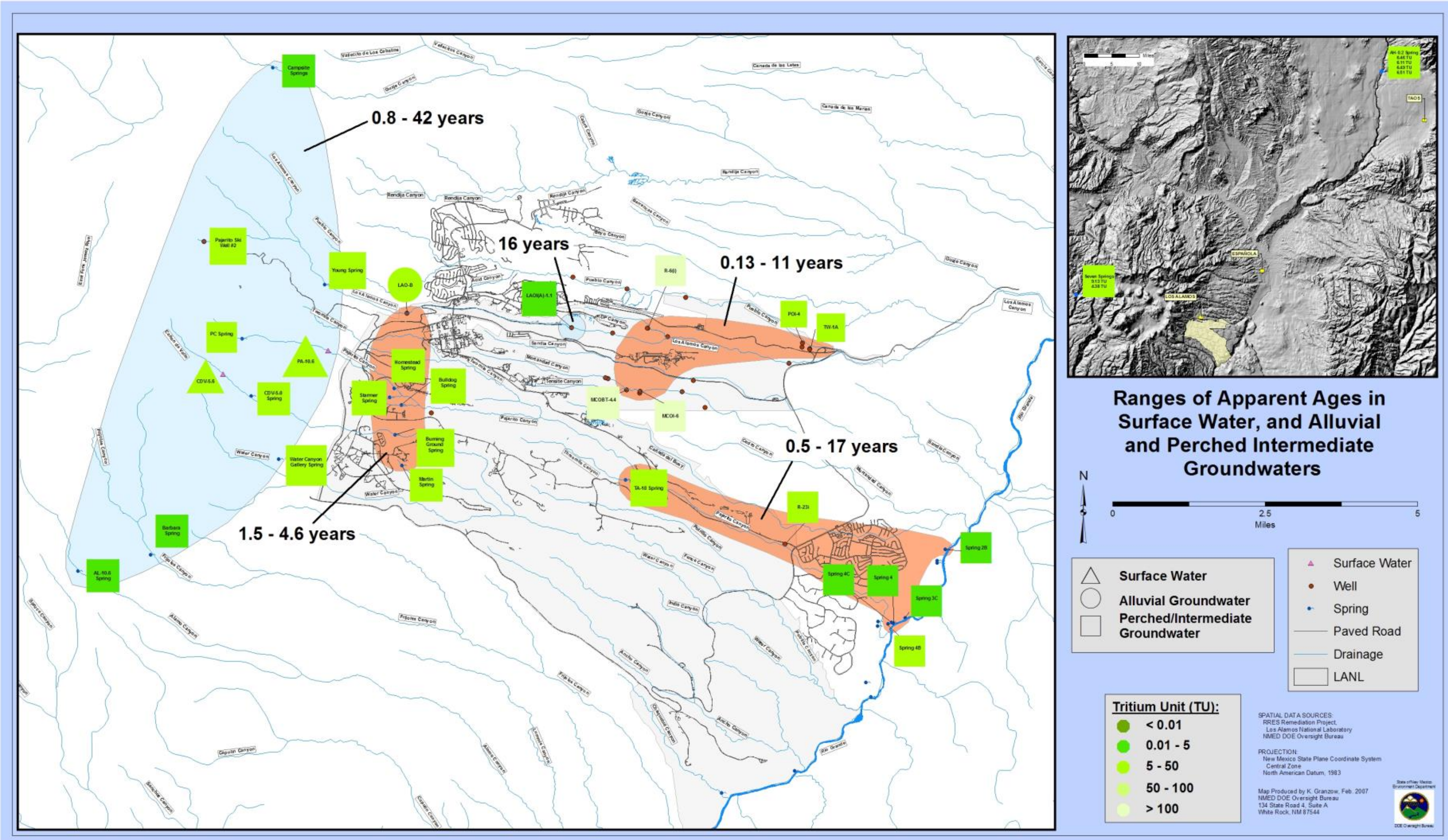



Figure 6-14. Distributions of average delta 18O (permil) versus delta 2H (permil) for groupings of White Rock Canyon Springs, alluvial groundwater (non-processed), LANL regional aquifer wells and springs, and surface water and springs discharging within the Sierra de los Valles, New Mexico. One standard deviations for delta18O and delta2H of samples are shown as error bars.



3H Range
0.4 - 27 TU
3H 1.8 TU
3H Range
7.7 - 6520 TU
3H Range
1.6 - 31.7 TU
3H Range
17 - 46 TU
Distributions of Tritium in Surface Water, and Alluvial and Perched Intermediate Groundwaters
N
0
2.5
5
Miles
Surface Water
Alluvial Groundwater
Perched/Intermediate Groundwater
Surface Water
Well
Spring
Paved Road
Drainage
LANL
Tritium Unit (TU):
< 0.01
0.01 - 5
5 - 50
50 - 100
> 100
SPATIAL DATA SOURCES:
RRES Remediation Project,
Los Alamos National Laboratory
NMED DOE Oversight Bureau
PROJECTION:
New Mexico State Plane Coordinate System
Central Zone
North American Datum, 1983
Map Produced by K. Granzow, Feb. 2007
NMED DOE Oversight Bureau
134 State Road 4, Suite A
White Rock, NM 87544


0.8 - 42 years
16 years
0.13 - 11 years
0.5 - 17 years
1.5 - 4.6 years
Ranges of Apparent Ages in Surface Water, and Alluvial and Perched Intermediate Groundwaters
N
0
2.5
5
Miles
Surface Water
Alluvial Groundwater
Perched/Intermediate Groundwater
Surface Water
Well
Spring
Paved Road
Drainage
LANL
Tritium Unit (TU):
< 0.01
0.01 - 5
5 - 50
50 - 100
> 100
Map Produced by K. Granzow, Feb. 2007
NMED DOE Oversight Bureau
134 State Road 4, Suite A
White Rock, NM 87544

# Atmospheric Tritium Input Curve and Perched Intermediate-Depth Groundwater

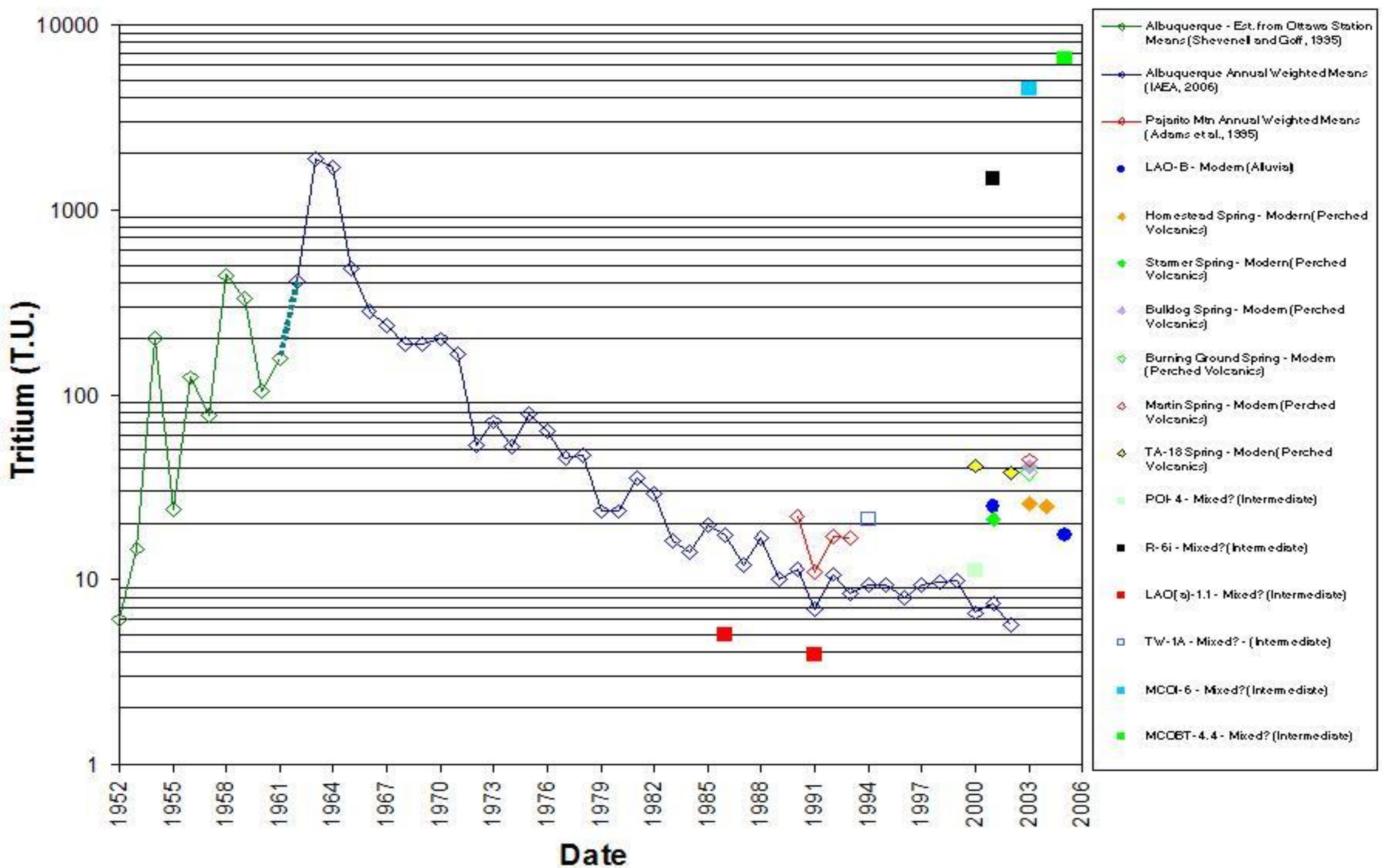
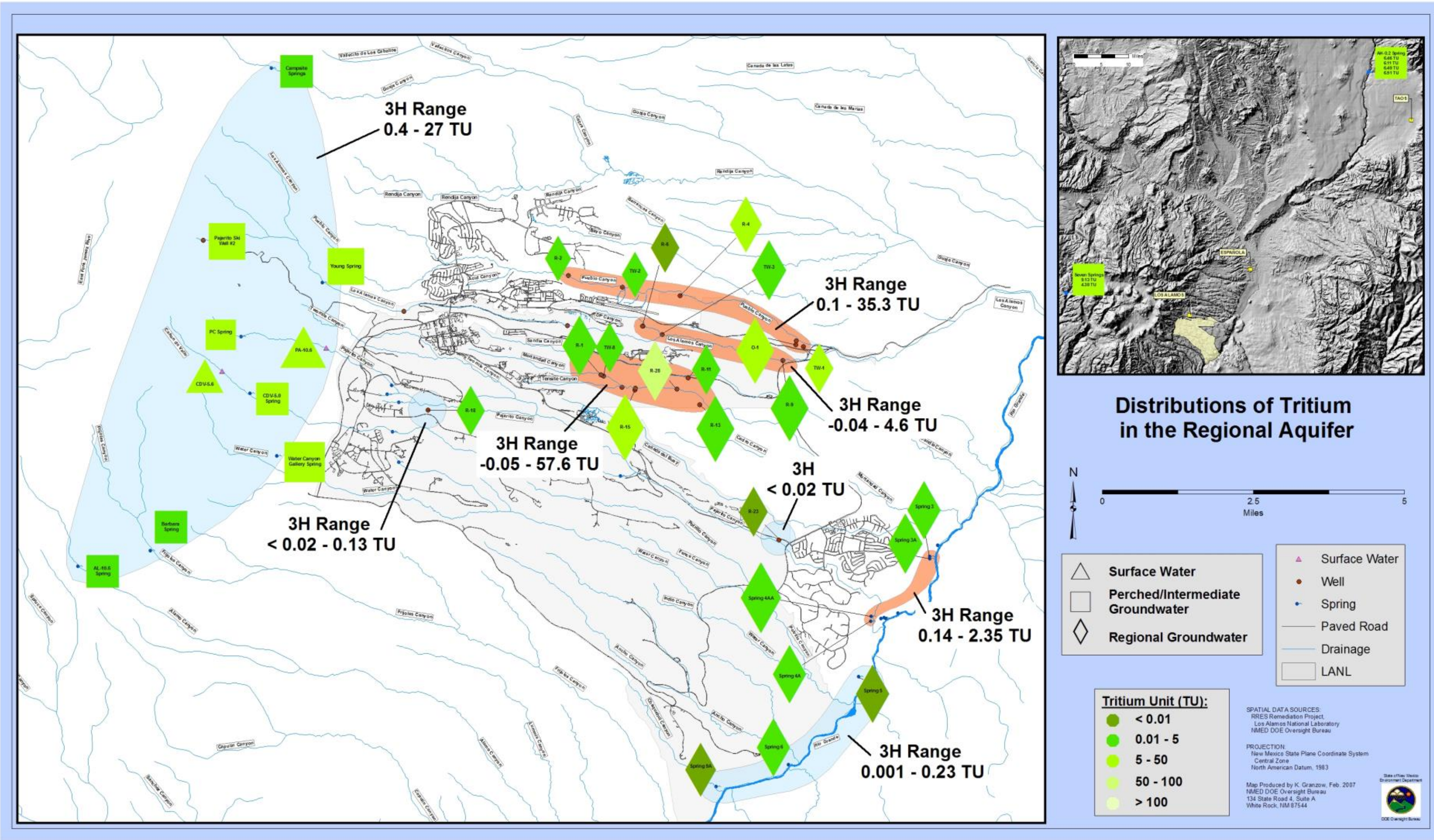
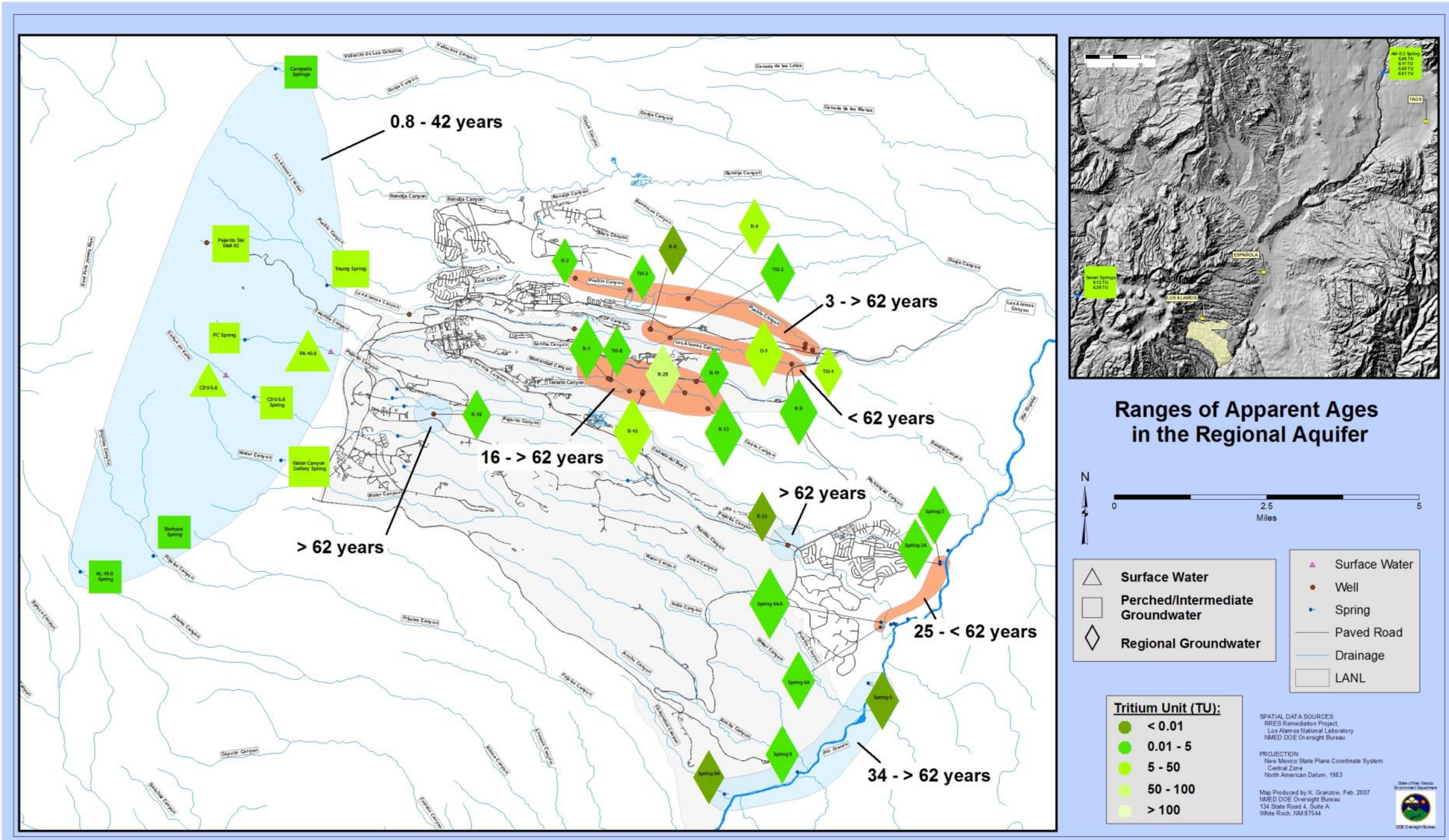
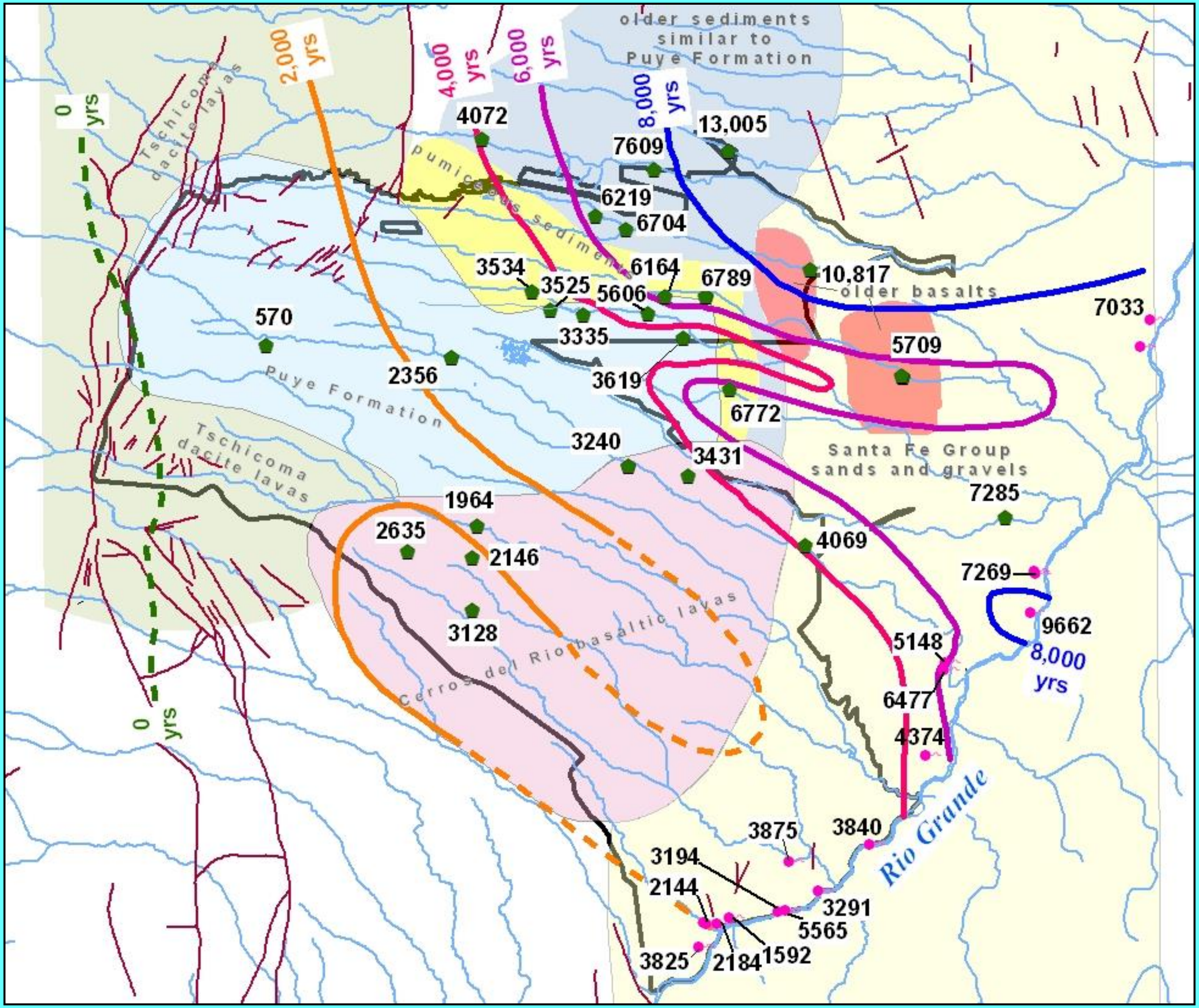



Figure 6-9. Atmospheric Tritium Curve and Initial Tritium Activities for Samples Collected Beneath the Pajarito Plateau - Perched Alluvial and Volcanics, and Intermediate Aquifers

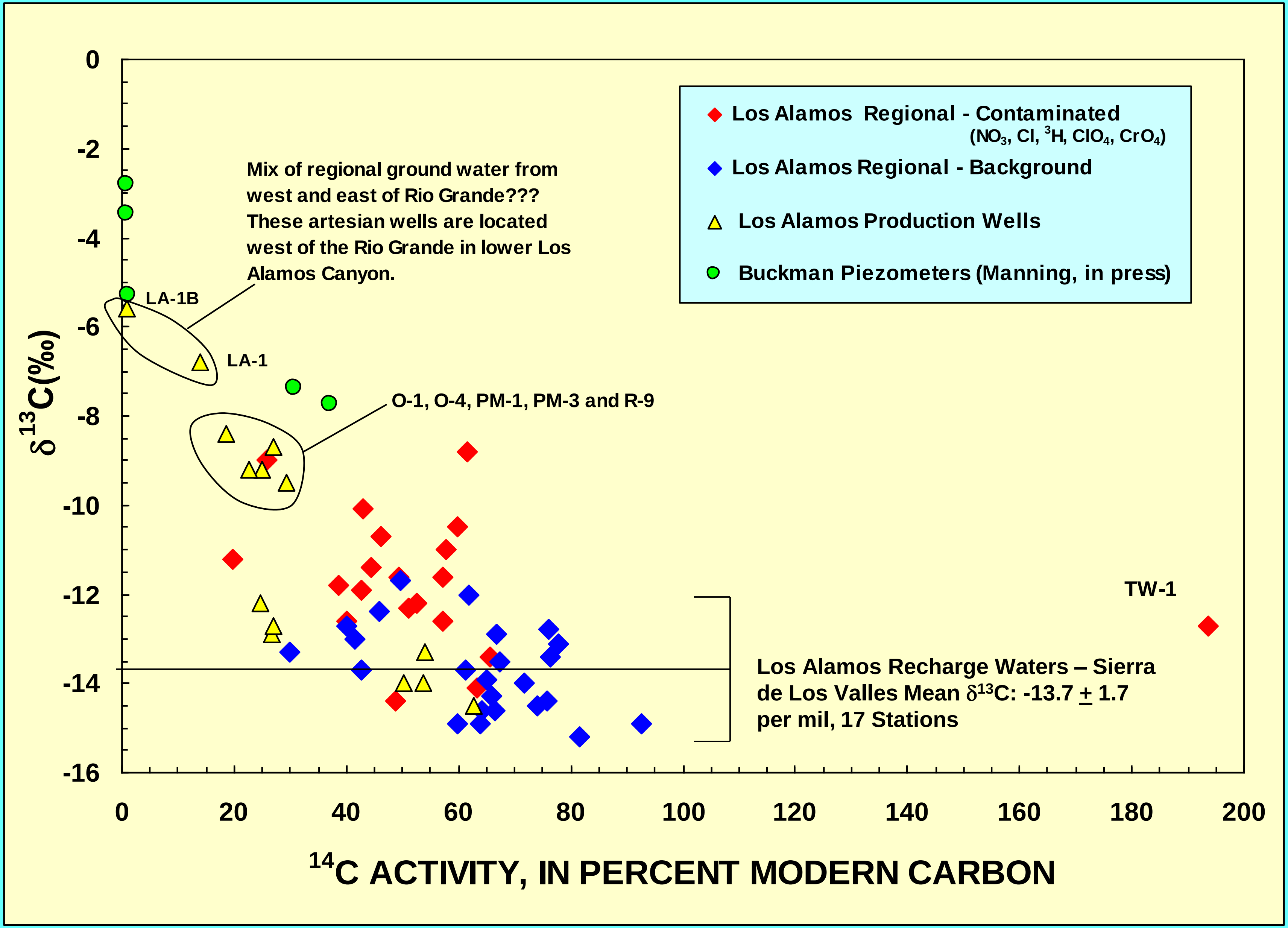

Distributions of Tritium in the Regional Aquifer
3H Range 0.4 - 27 TU
3H Range 0.1 - 35.3 TU
3H Range -0.04 - 4.6 TU
3H Range -0.05 - 57.6 TU
3H < 0.02 TU
3H Range < 0.02 - 0.13 TU
3H Range 0.14 - 2.35 TU
3H Range 0.001 - 0.23 TU
Surface Water
Perched/Intermediate Groundwater
Regional Groundwater
Surface Water
Well
Spring
Paved Road
Drainage
LANL
Tritium Unit (TU):
< 0.01
0.01 - 5
5 - 50
50 - 100
> 100
N
0
2.5
5
Miles


Ranges of Apparent Ages in the Regional Aquifer
0.8 - 42 years
3 - > 62 years
< 62 years
16 - > 62 years
> 62 years
> 62 years
25 - < 62 years
34 - > 62 years
Surface Water
Perched/Intermediate Groundwater
Regional Groundwater
Surface Water
Well
Spring
Paved Road
Drainage
LANL
Tritium Unit (TU):
< 0.01
0.01 - 5
5 - 50
50 - 100
> 100
N
0
2.5
5
Miles
SPATIAL DATA SOURCES:
RRES Remediation Project,
Los Alamos National Laboratory
NMED DOE Oversight Bureau
PROJECTION:
New Mexico State Plane Coordinate System
Central Zone
North American Datum, 1983
Map Produced by K. Granzow, Feb. 2007
NMED DOE Oversight Bureau
134 State Road 4, Suite A
White Rock, NM 87544
Campsite Springs
Pajarito Ski Well #2
Young Spring
PC Spring
PA-10.6
CDV-5.6
CDV-5.8 Spring
Water Canyon Gallery Spring
Barbara Spring
AL-16.6 Spring
R-2
R-6
R-4
TW-2
TW-3
R-1
TW-8
R-25
R-11
O-4
TW-4
R-18
R-15
R-13
R-9
R-22
Spring 2
Spring 3A
Spring 4AA
Spring 6A
Spring 5
Spring 6
Spring 8A
ESPANOLA
LOS ALAMOS
TAOS

# Unadjusted Radiocarbon Ages of DIC and Geology near the Regional Aquifer Water Table, Pajarito Plateau, New Mexico



# Carbon-14 (Percent Modern Carbon) Versus $\delta^{13}C$, Pajarito Plateau and Surrounding Area, New Mexico



# Sandia Canyon, New Mexico

Over 15 years of Cr(VI) release from the TA-03 cooling tower.

Between 31,000 and 72,000 kg of Cr(VI) were released between 1956 and 1972.

Most of the Cr(VI) is from dissociation of potassium dichromate ($K_2Cr_2O_7$).

Sandia Canyon wetland

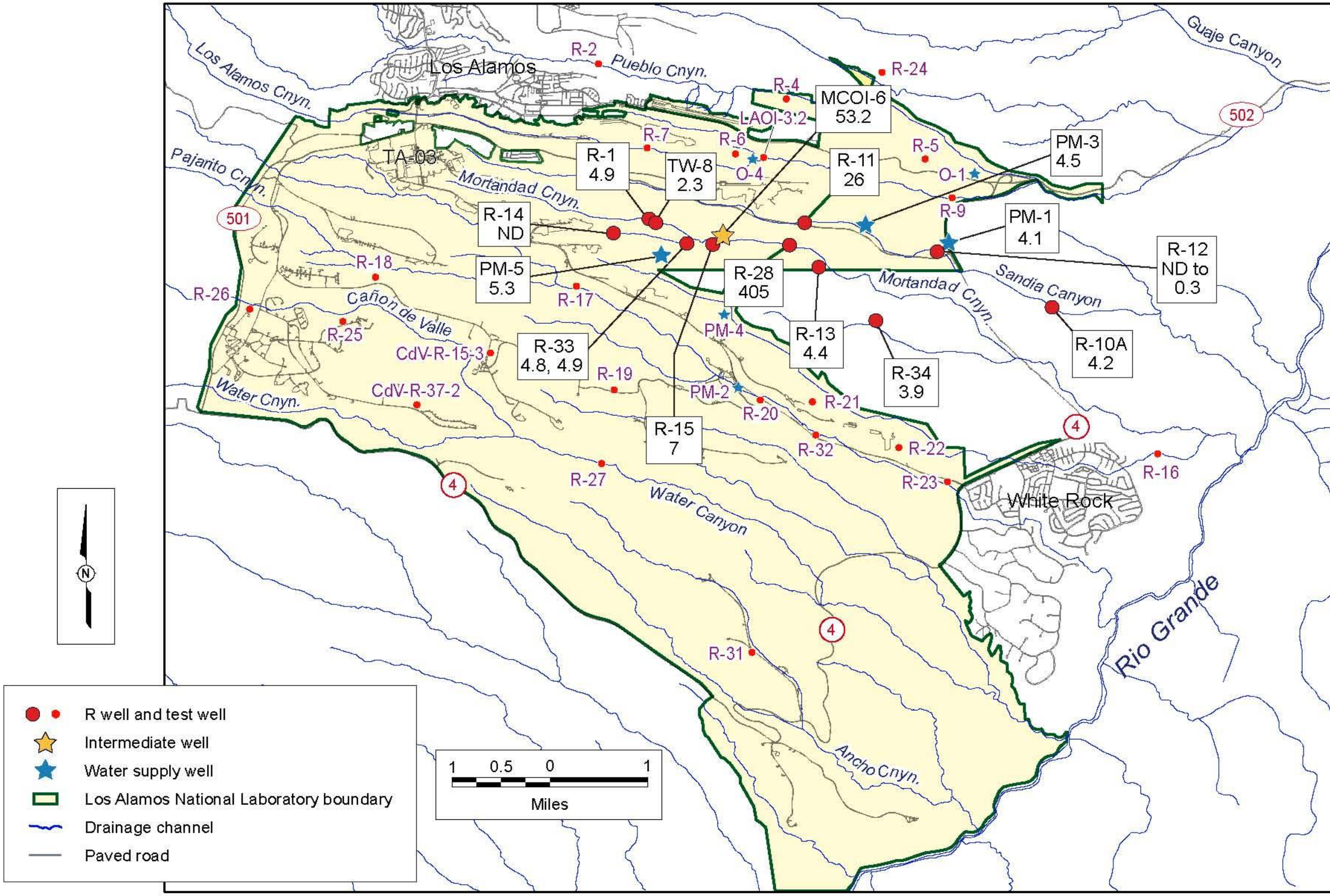
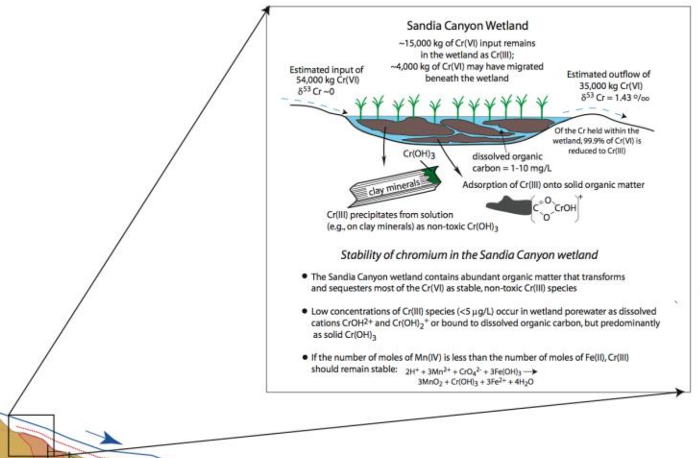
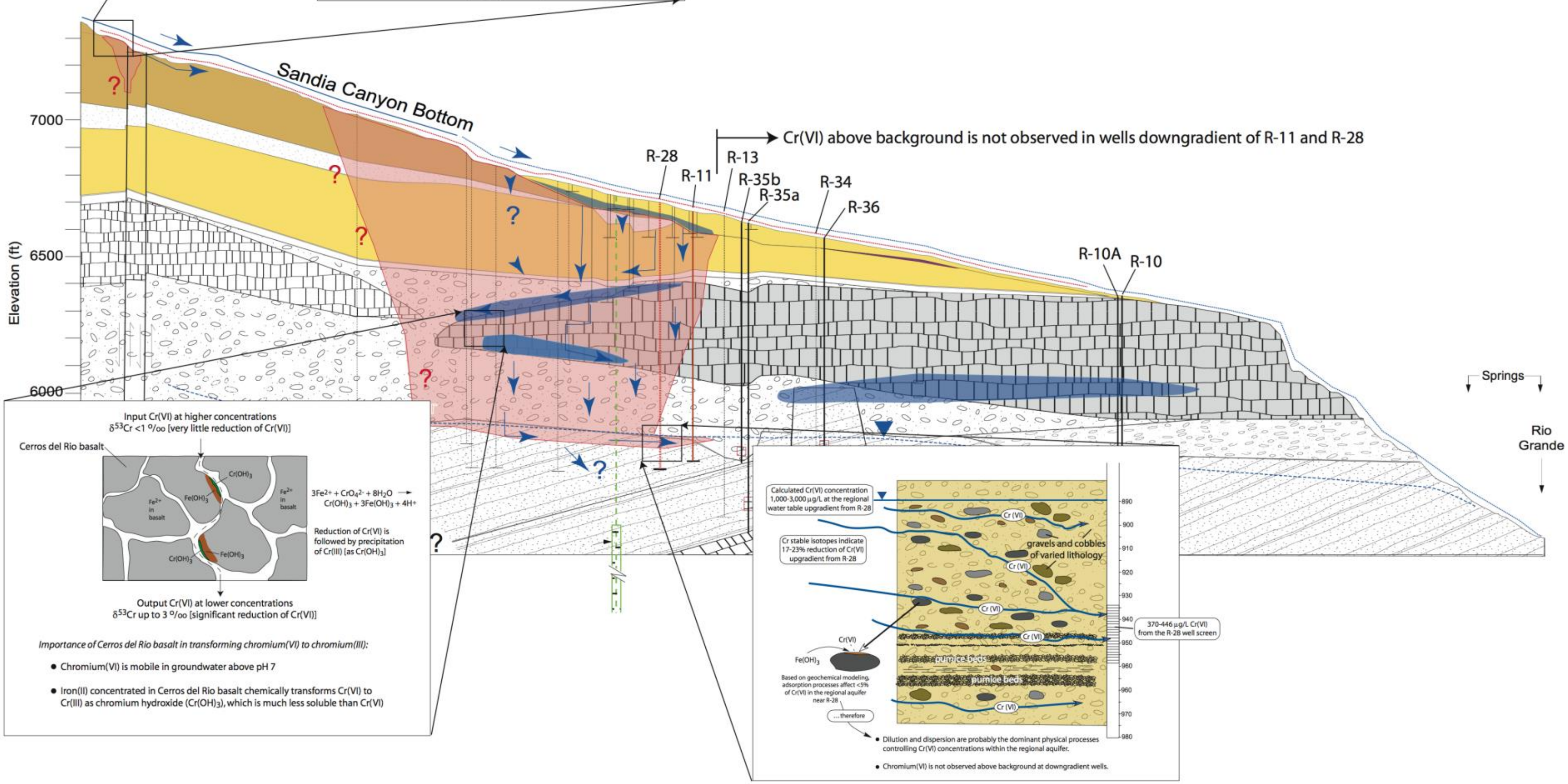



**Figure 3-2. Dissolved hexavalent chromium concentrations (in µg/L) in regional and intermediate wells**

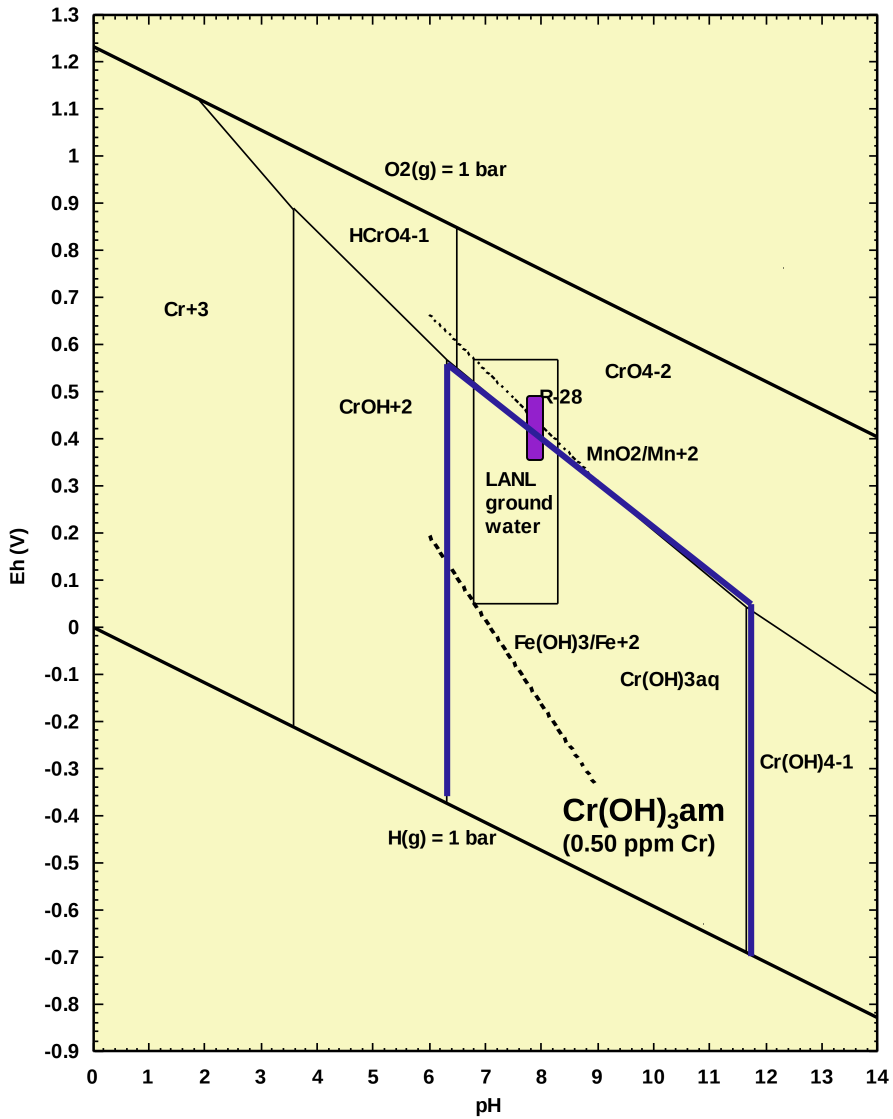
# Geochemical Conceptual Model for Chromium Fate and Transport Pajarito Plateau, New Mexico


Patrick Longmire and Jeffrey Heikoop
EES-6, LANL

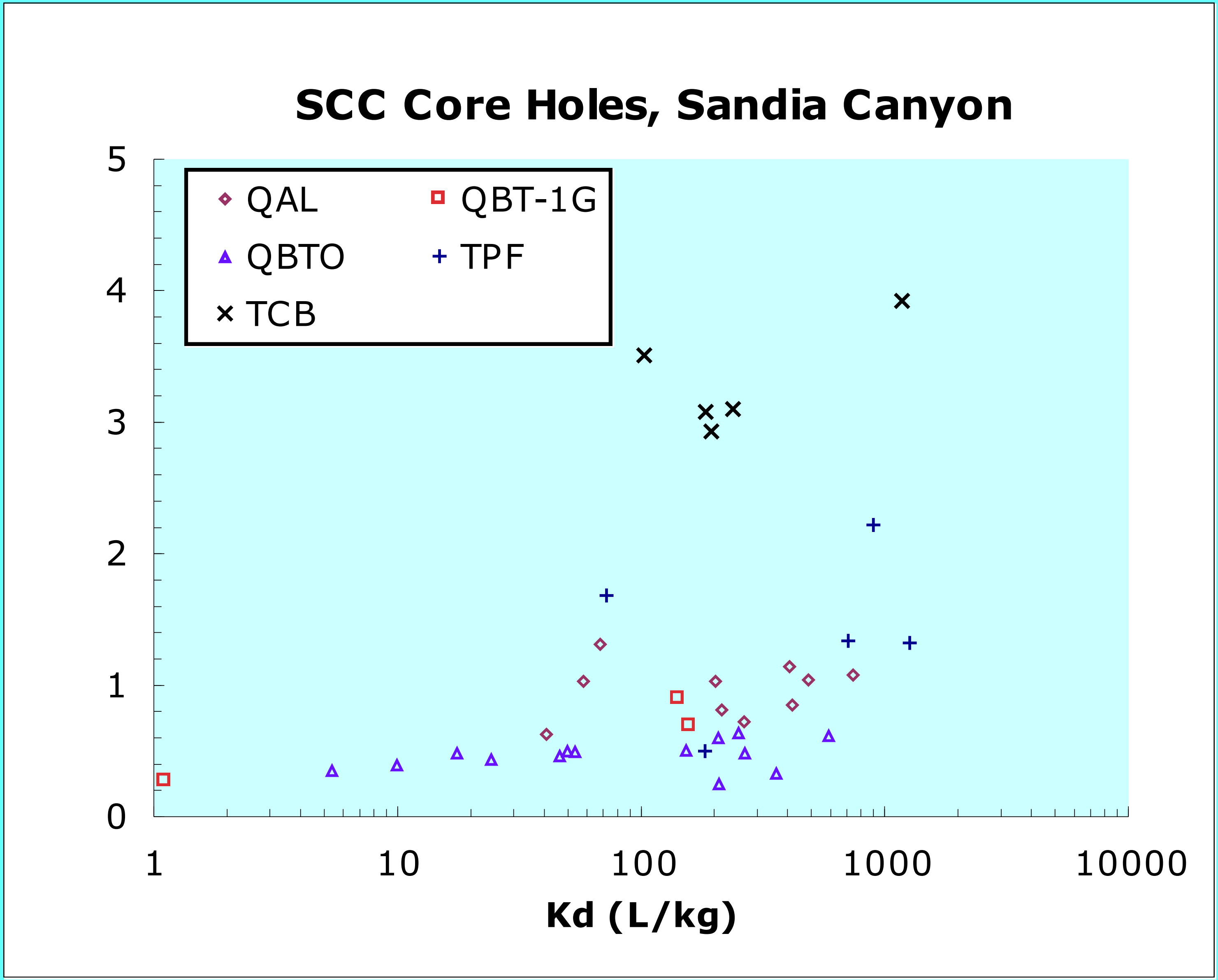



# Oxidation-Reduction Conditions for Chromium in Aqueous Solutions




Eh-pH diagram for part of the Cr-Mn-Fe-O-H system at 25C and 1 bar. Log concentrations of total dissolved Fe and Mn = -4.75 and -4.74 molal, respectively.


SCC Core Holes, Sandia Canyon
QAL
QBT-1G
QBTO
TPF
TCB
0
1
2
3
4
5
1
10
100
1000
10000
Kd (L/kg)

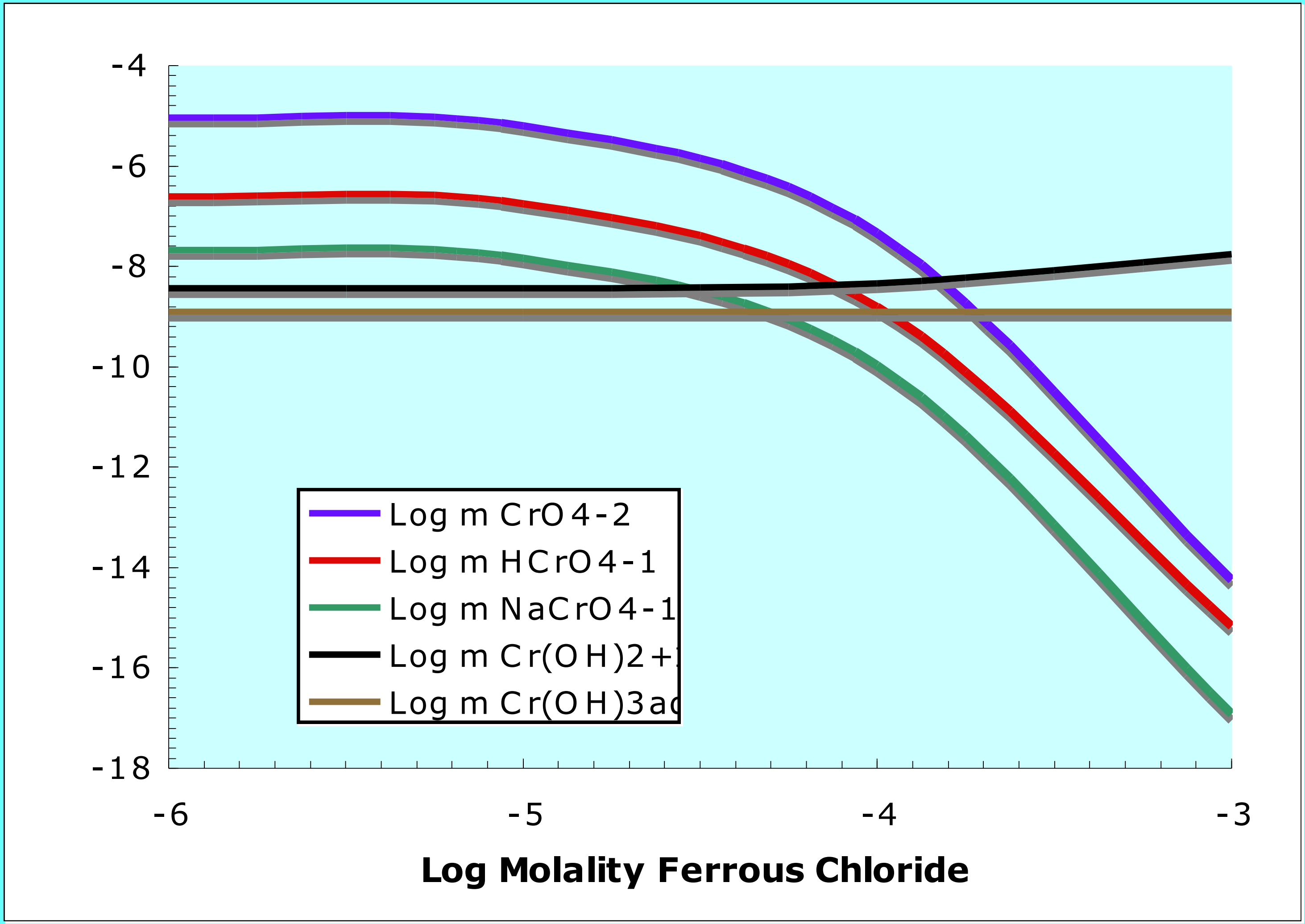
# Groundwater Remediation of Chromium(VI)

*Chemical Reduction with Ferrous Chloride*

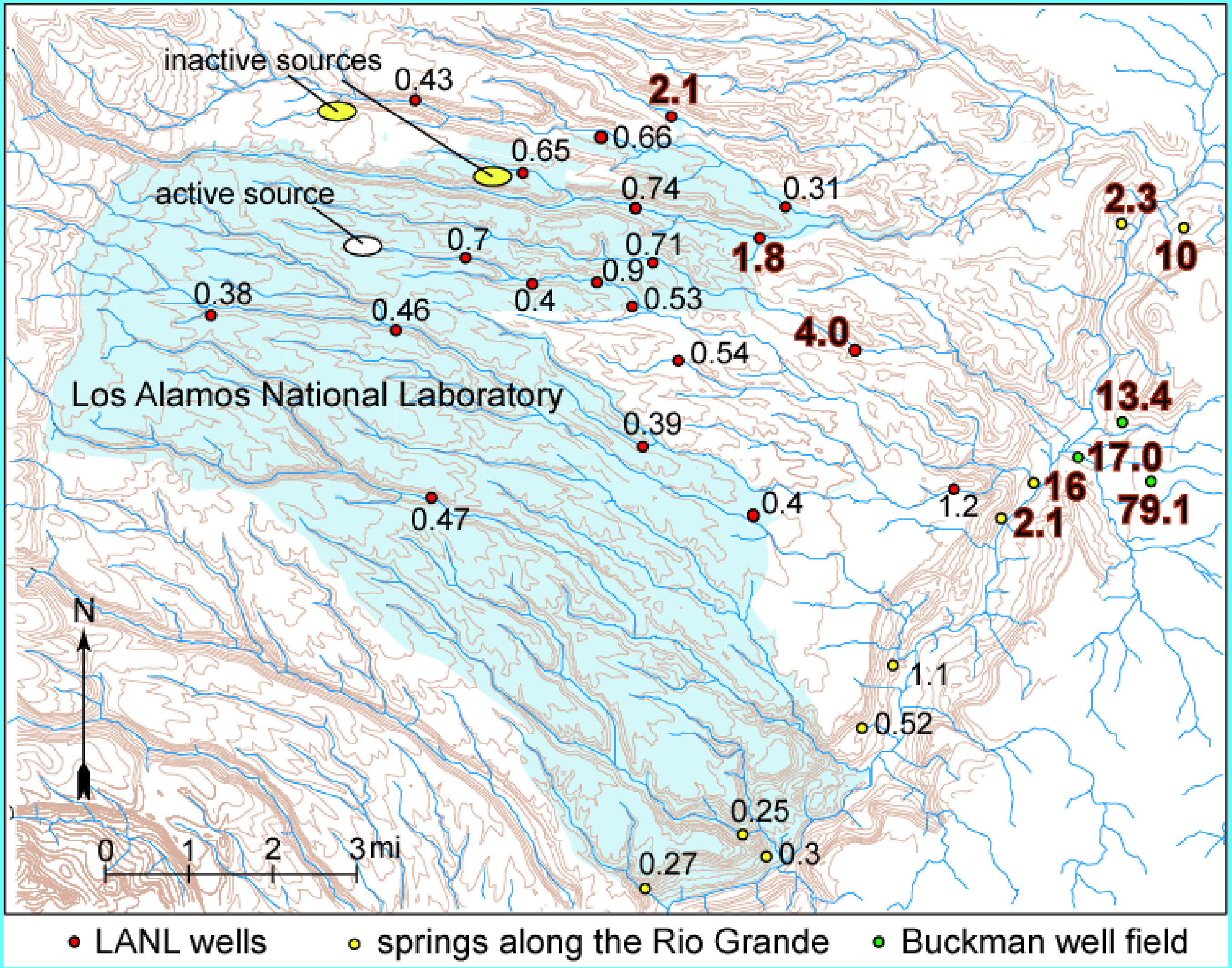
$$CrO_4^{2-} + 3FeCl_2 + 8H_2O =$$
$$Cr(OH)_3am + 3Fe(OH)_3am + 6Cl^- + 4H^+$$

Addition of $CaCO_3$ or $Ca(OH)_2$ is required to maintain neutral pH conditions depending on the buffering capacity of the aquifer.

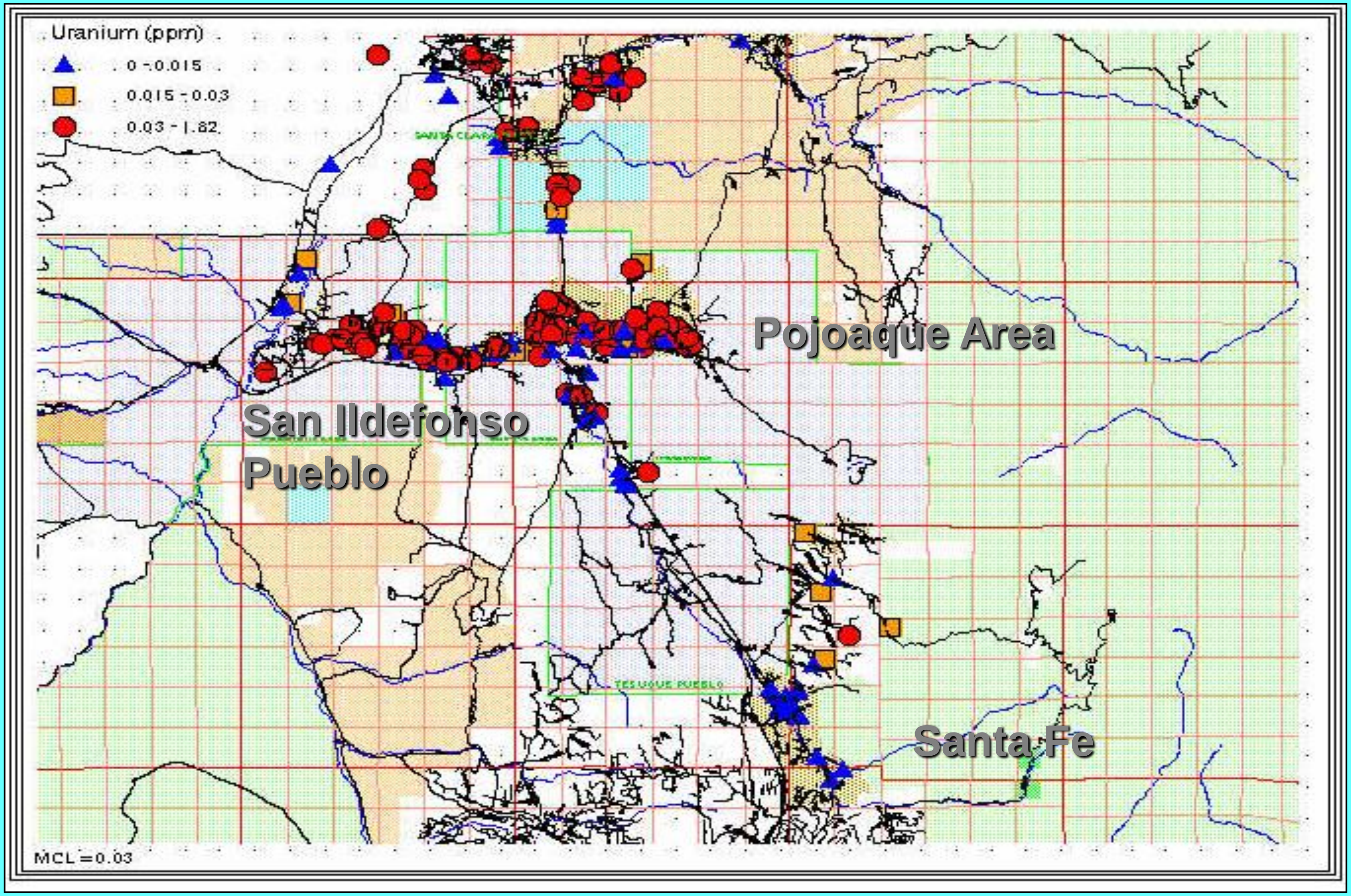
# Results of Geochemical Modeling (PHREEQC2.2) Reacting R-28 Groundwater with Ferrous Chloride in Equilibrium with Calcite



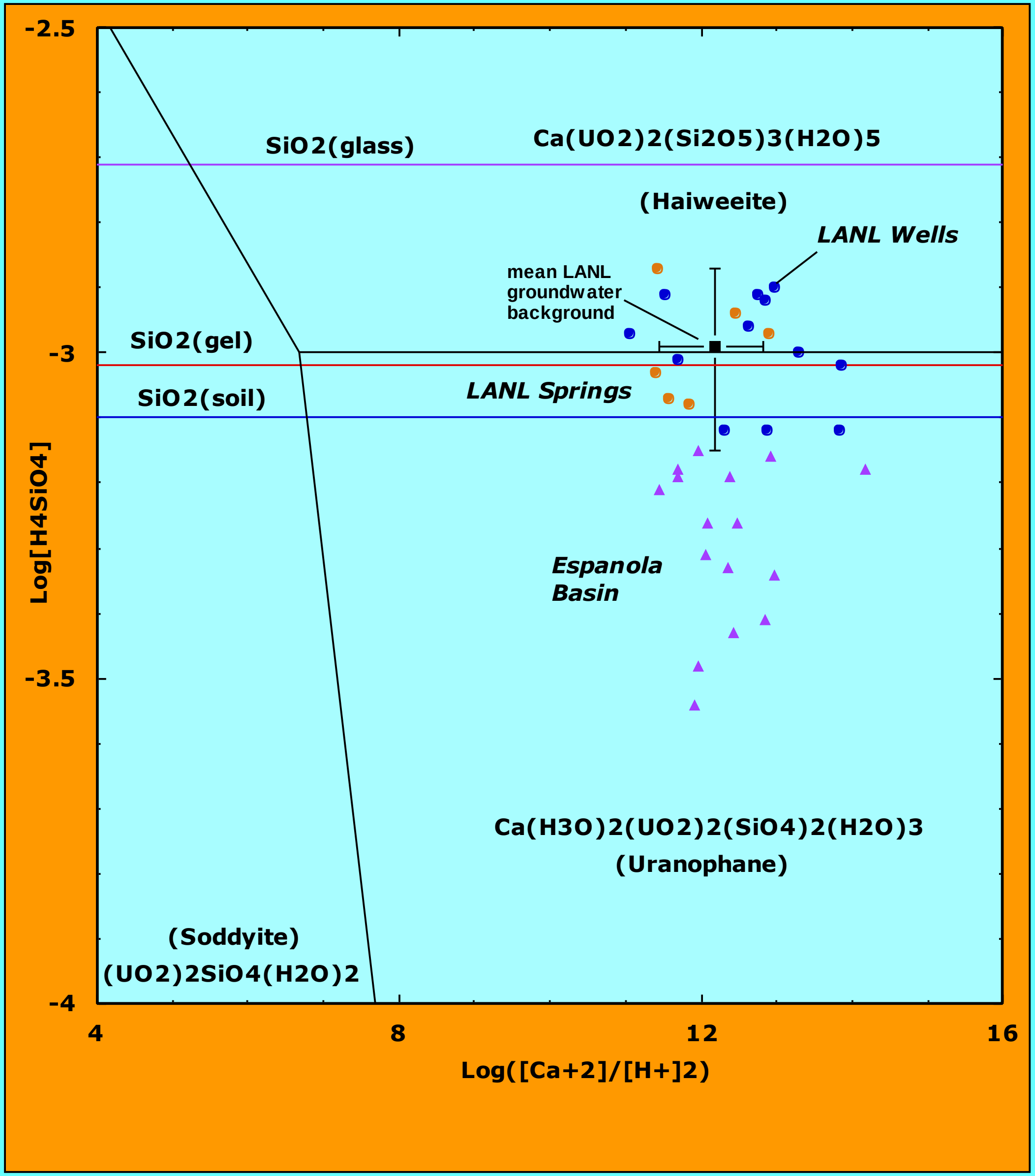
# Mean Concentrations of Dissolved Uranium (μg/L) in the Regional Aquifer from 2005 through 2007, Pajarito Plateau (1 to 5 samples per location, mean background = 0.63 μg/L)



# Uranium Concentrations in Groundwater, Española Basin, New Mexico



# Log $[H_4SiO_4]$ Versus Log $([Ca^{2+}]/[H^+]^2)$ Diagram at 25ºC and 1 Bar Pressure for the Regional Aquifer, Los Alamos and the Española Basin, New Mexico



# Summary and Conclusions

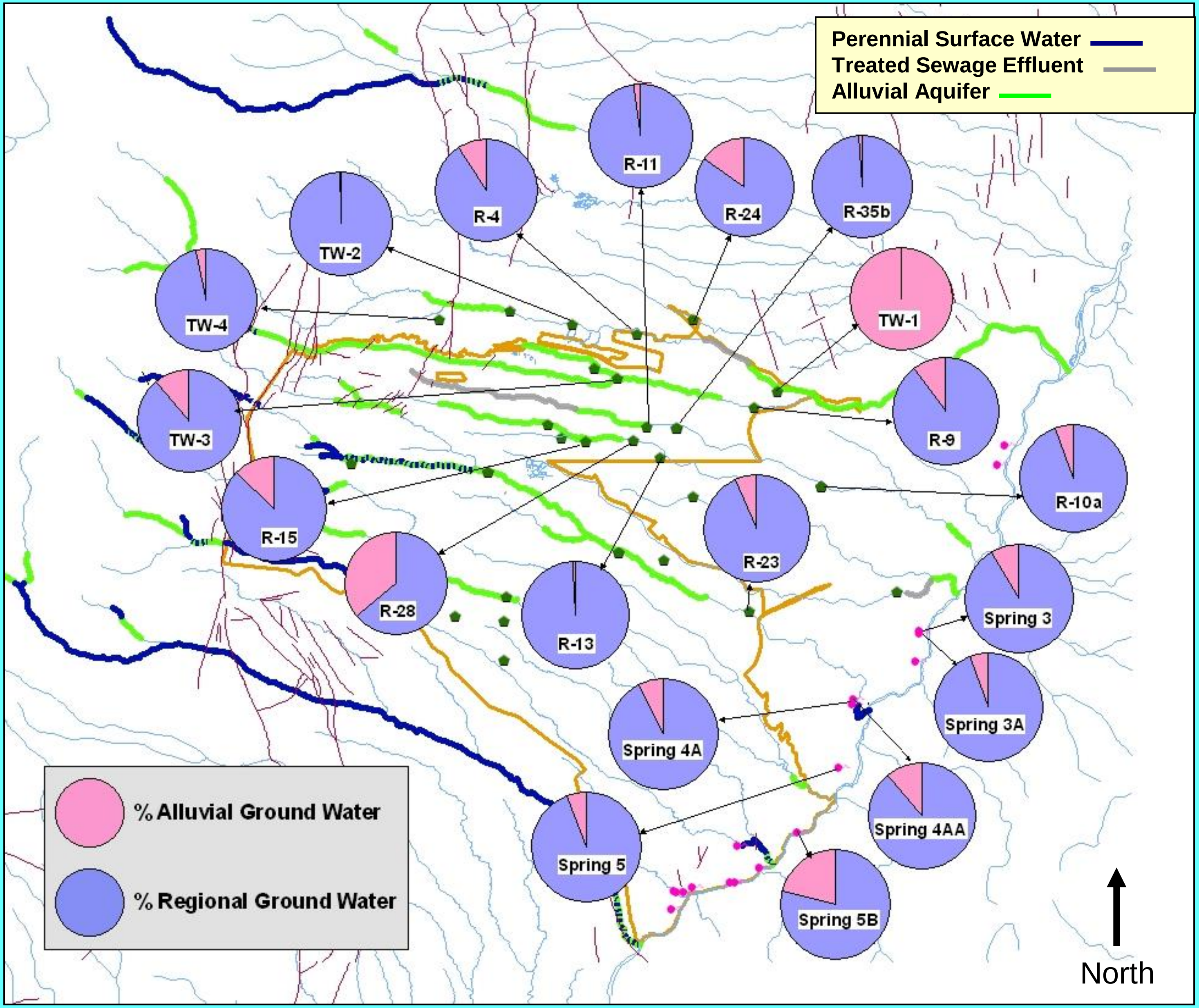
- Groundwater can have a mixed age, containing modern and submodern components.
- Variations in unadjusted $^{14}C$ ages (570 to 13,005 years) for the regional aquifer result from sources of recharge water, mixing of waters, and hydraulic properties of the aquifer material.
- Application of $^{14}C$ ages with mobile chemicals such as tritium and chloride define preferred groundwater flow paths within the regional aquifer.

# Summary and Conclusions

- Transport of chromium(VI) is likely under relatively oxidizing and basic pH conditions.
- Dissolved concentrations of uranium(VI) are less than 2.52e-08 molar (6 $\mu$g/L) within the regional aquifer.
- Much higher concentrations of natural uranium (up to 7.65e-03 molar, 1820 $\mu$g/L) are observed east of the Rio Grande.

# Supplemental Material

# Average Mixing Ratios for the Regional Aquifer Containing Chloride from Alluvial Ground Water, Pajarito Plateau, New Mexico



# Atmospheric Tritium Input Curve and White Rock Canyon Springs

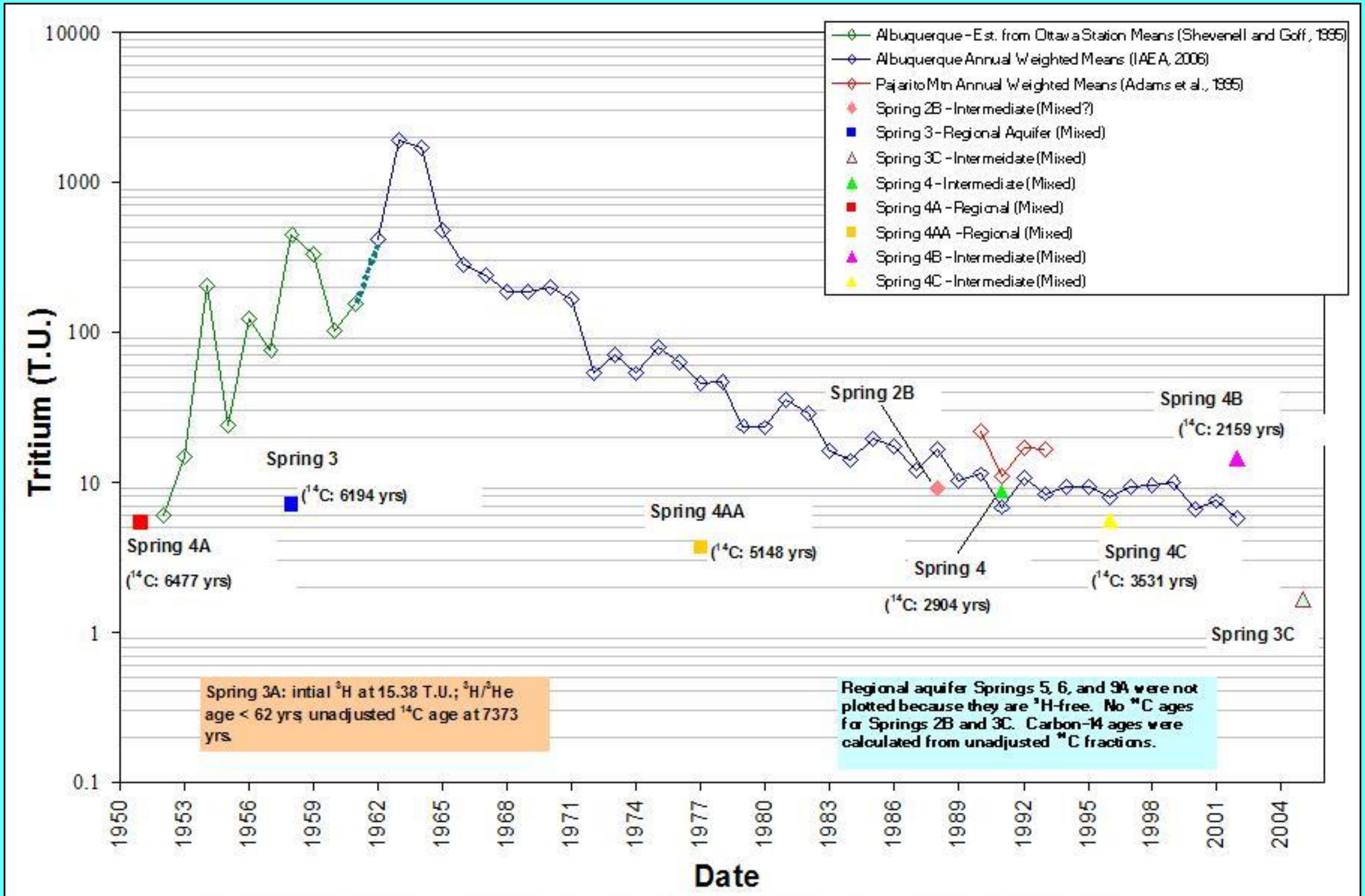
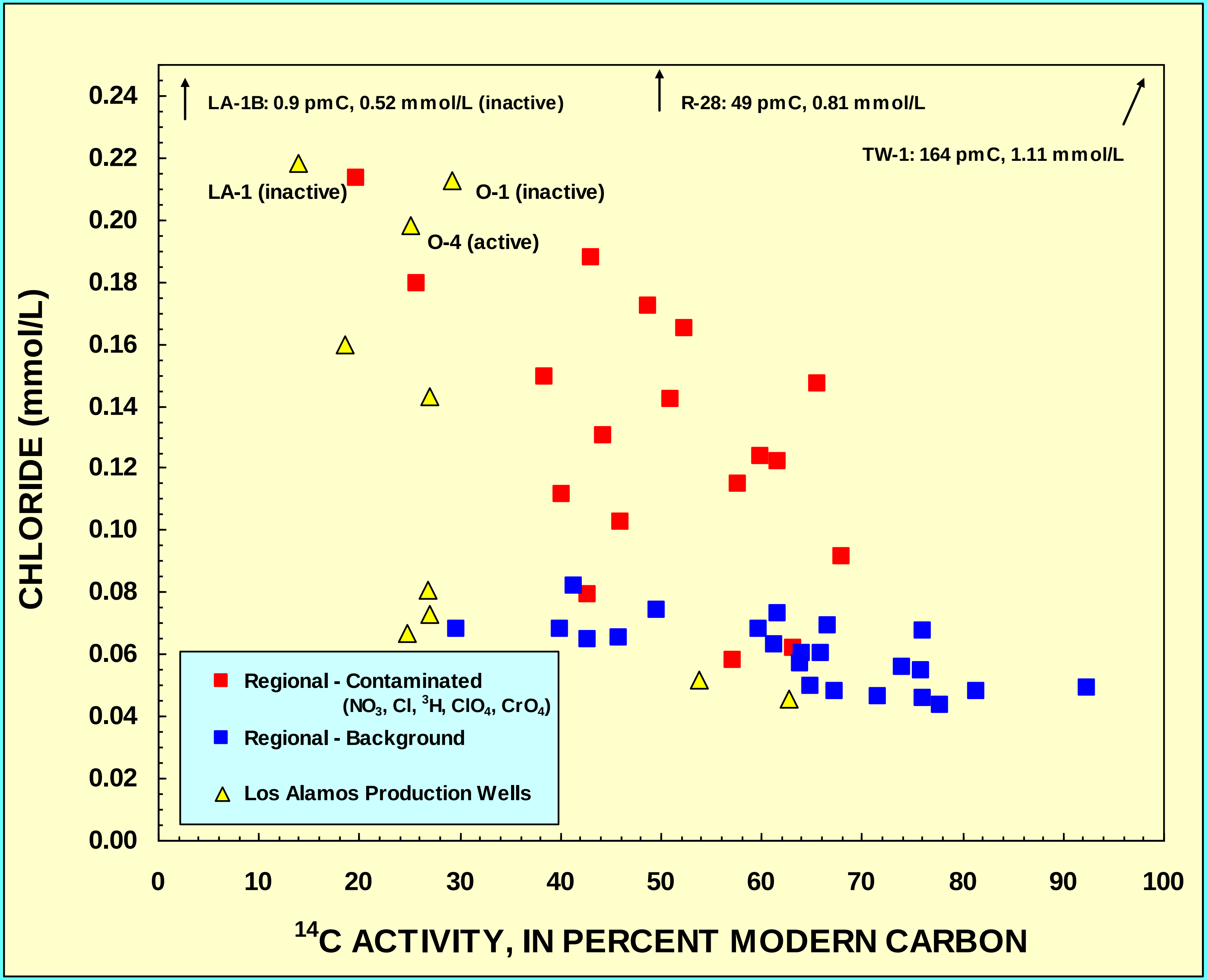
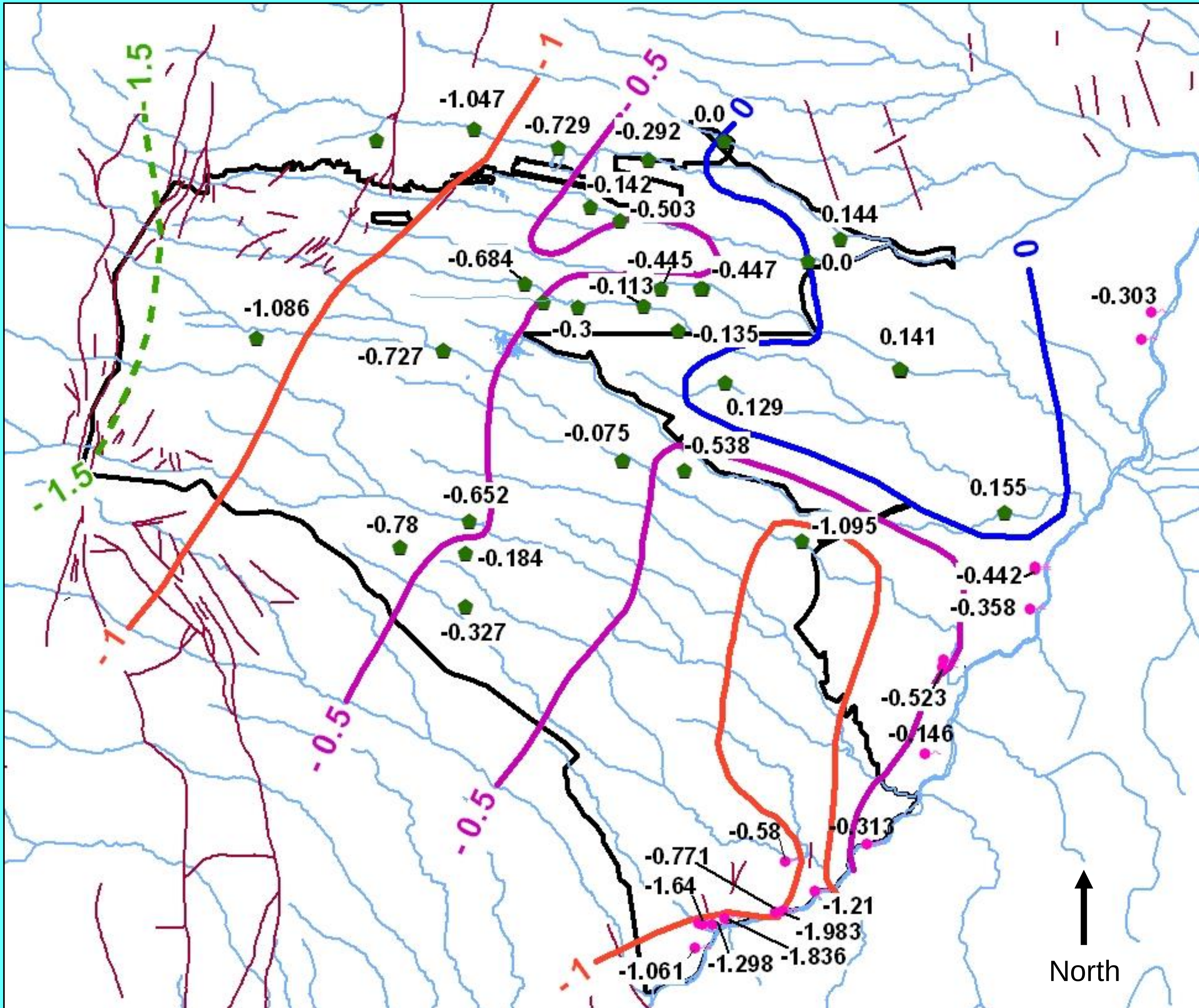



Figure 6-15. Atmospheric Tritium Curve and Initial Tritium Activities for Samples Collected at the White Rock Canyon springs

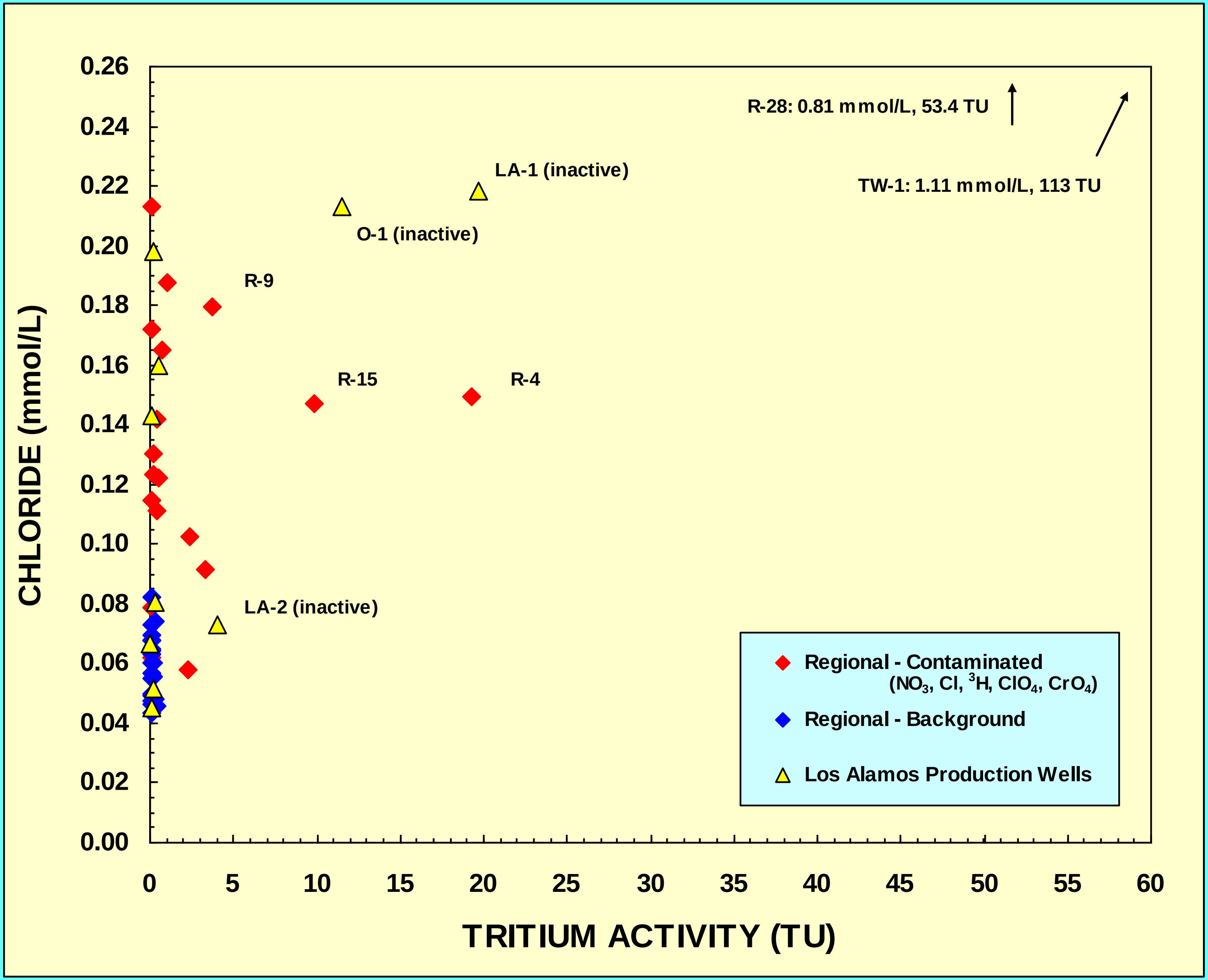
# Carbon-14 (Percent Modern Carbon) Versus Chloride (mmol/L), Los Alamos, New Mexico



# Saturation Index Map for $CaCO_3$ (Calcite) for the Regional Aquifer

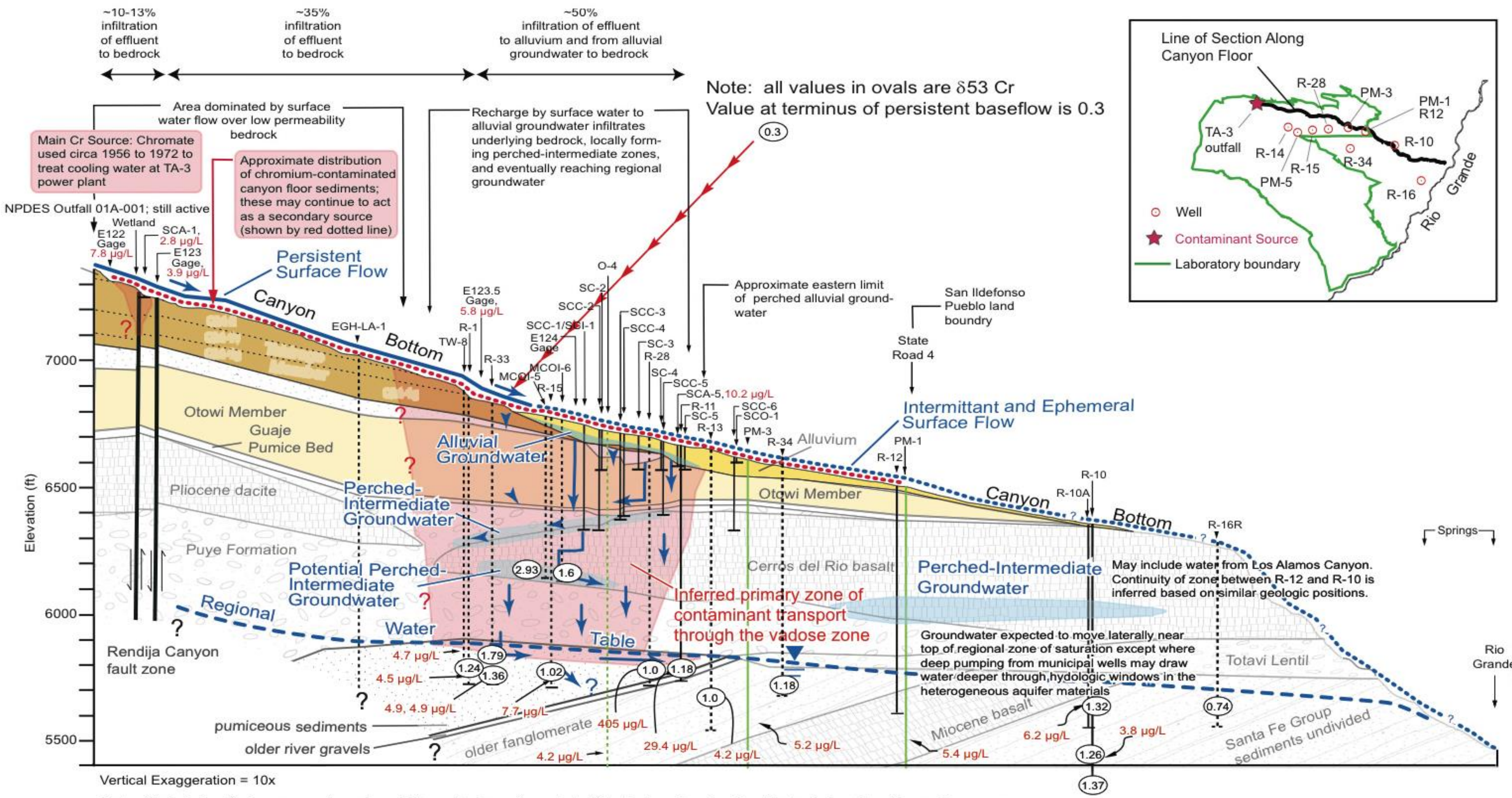


# Tritium (TU) Versus Chloride (mmol/L), Los Alamos, New Mexico



# Chromium and Uranium

- Speciation
- Adsorption
- Mineral Equilibrium
- Groundwater Remediation (Chromium)




Note: Wells in Sandia Canyon are shown by solid lines. Nearby wells projected into the line of section from Mortandad and Los Alamos Canyons are shown as dashed lines. Water supply wells are shown in green. The line of section follows the Sandia Canyon stream channel. Most recent data for chromium concentrations in filtered surface water, alluvial groundwater, perched-intermediate groundwater, and regional groundwater are shown in red. Multiple concentrations are shown in cases where intermediate and regional wells have more than one well screen, (e.g. R-12 and R-33).

Disclaimer: This map was created for work processes associated with the Interim Measures Investigation Report for Chromium Contamination in Groundwater. All other uses for this map should be confirmed with the LANL Environmental Programs Directorate.

**Figure 6.0-1. Conceptual hydrogeologic cross section showing potential chromium transport pathways and dissolved hexavalent chromium values (µg/L) for surface water, monitoring wells, and water supply wells in the vicinity of Sandia Canyon**

# Background Total Dissolved Cr and Cr(VI) Concentrations (μg/L), Los Alamos, New Mexico

*Regional Aquifer*

| Chemical | Range | Mean | $1\sigma$ |
|---|---|---|---|
| Cr[1] | 0.4 to 7.2 | 3.1 | ±1.6 |
| Cr(VI)[2] | 3.9 to 5.3 | 4.6 | ±0.5 |

[1]Upper Tolerance Limit (95th confidence interval, 95th percentile) = 5.75 μg/L. Number of samples = 80

[2]Number of samples = 9

# Soil Leaching Method

**Drying Time Soil**

110$^{o}$C for 16 hours in pre-weighed glass bottles

**Soil : Deionized Water Ratio**

50 mg dry soil to 75 mL of deionized $H_2O$

**Contact-Reaction Time**

48 hours in 125 mL Erlenmeyer flasks

Decanted into 50 mL centrifuge tubes for 30 minutes

**Filtering**

0.25 micrometer membranes

# Porewater Chemistry of SCC-2, Bandelier Tuff
## (Sample collected from 20.0 to 24.0 ft, pH = 8.10)

| **Analyte** | **Millimoles/Liter** | **Milligrams/Liter** |
|---|---|---|
| Ca | 0.30 | 12.2 |
| Mg | 0.10 | 2.52 |
| Na | 4.83 | 111 |
| K | 3.05 | 119 |
| Cl | 2.99 | 106 |
| $SO_4$ | 1.80 | 173 |
| $HCO_3$ (calculated) | 1.09 | 66.4 |
| $PO_4$ | 0.20 | 18.7 |
| F | 1.41 | 26.8 |
| $SiO_2$ | 7.50 | 450 |
| Cr | 0.03 | 1.33 |
| Fe | 0.07 | 4.18 |

# *Surface Complexation of Chromium(VI) Species*

$CrO_4^{2-}$


$[Fe^{+}...CrO_4^{2-}]^{-}$

$K_2$: $FeOH + CrO_4^{2-} - H_2O + H^{+} = FeCrO_4^{-}$ ; $\log K_2 = 10.82$

$OH\cdots CrO_4^{2-}$

$K_3$: $FeOH + CrO_4^{2-} = FeOHCrO_4^{2-}$ ; $\log K_3 = 3.9$ (estimated)

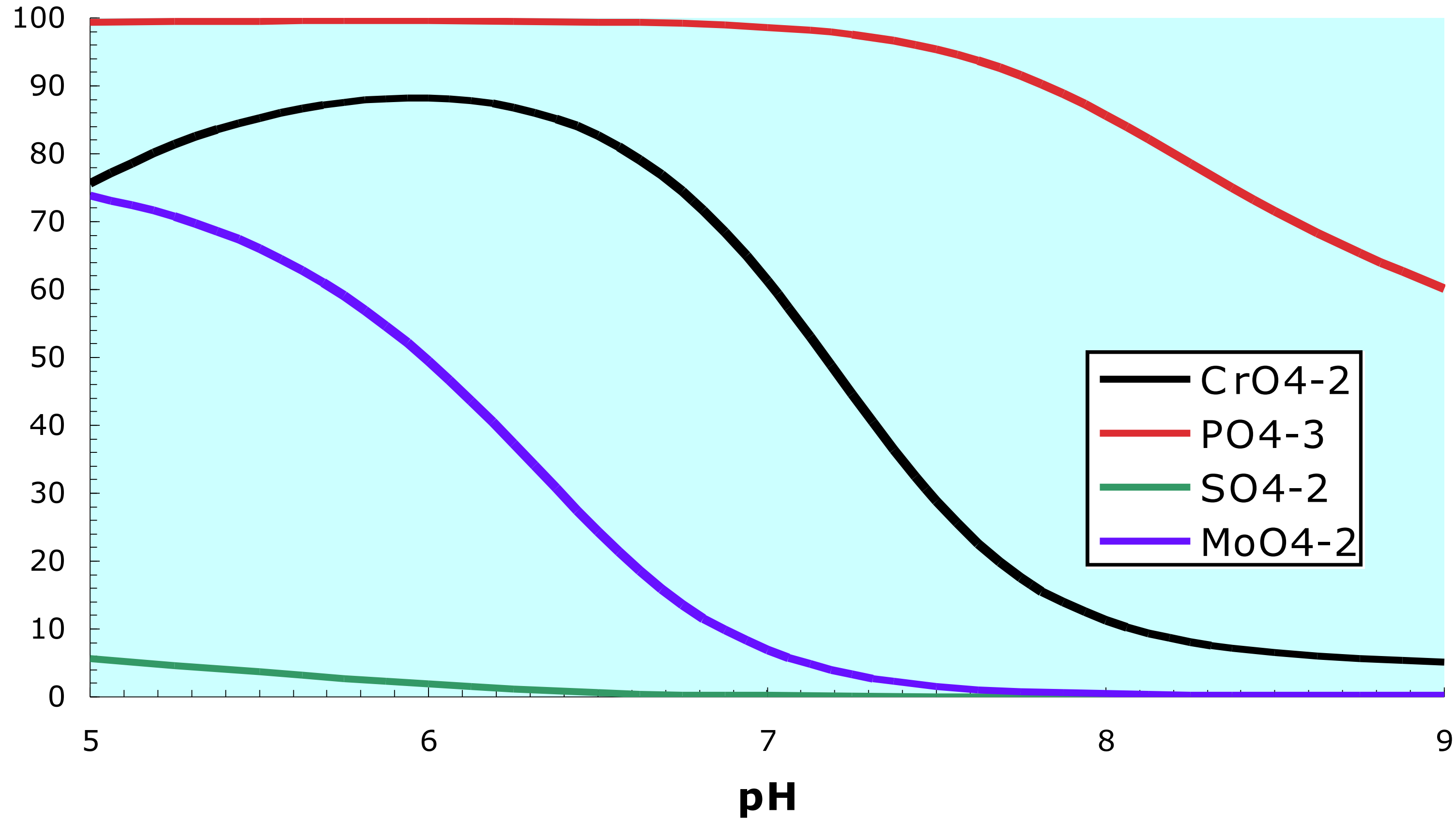
$Fe(OH)_3$

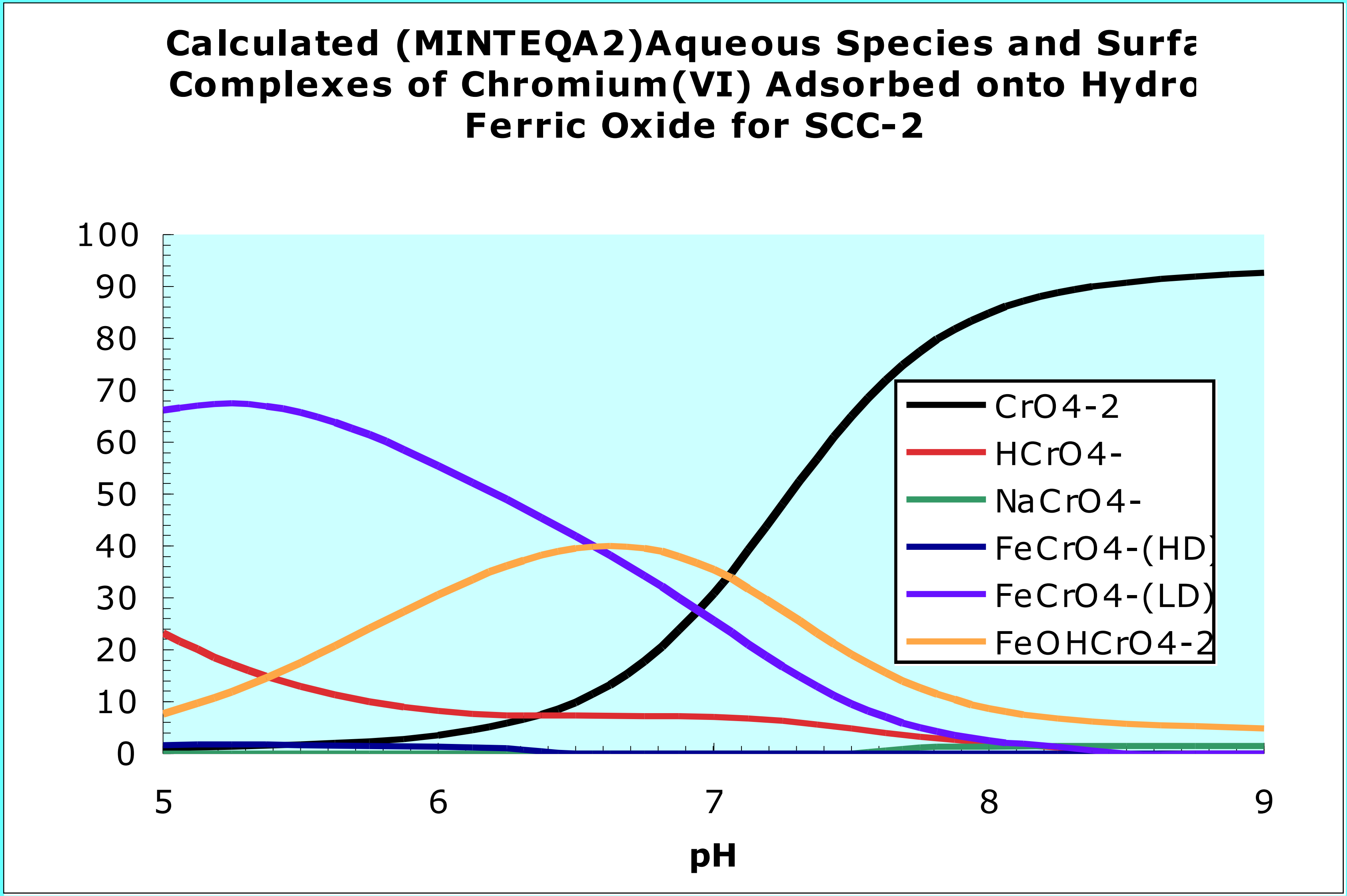
HFO

"hydrous ferric oxide"

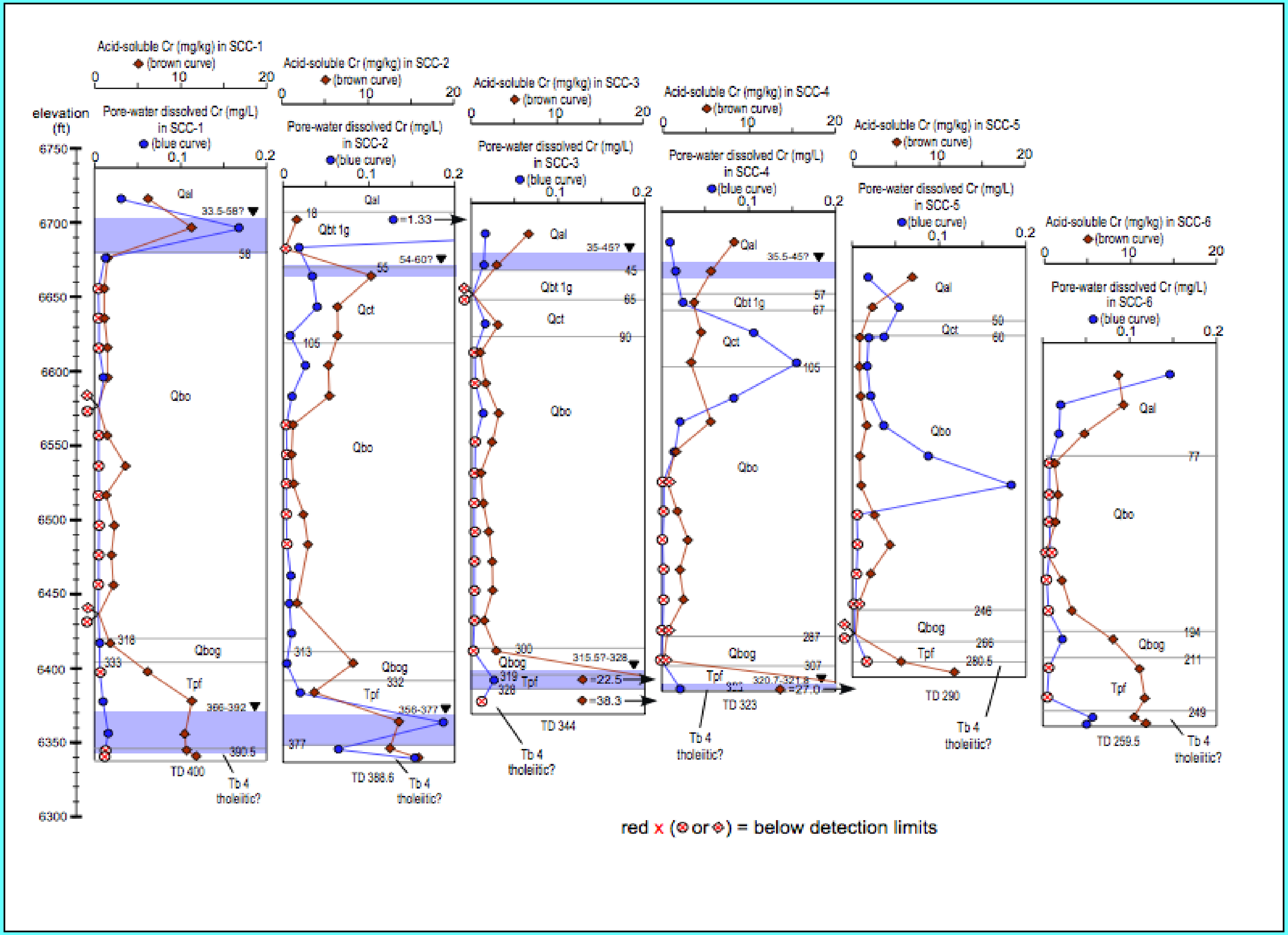
$HCrO_4^{-}$

**Calculated Adsorption Edge Plot ( MINTEQA2) for SCC-2 (log Cr = -4.55 m, log SO4 = -2.74 m, log PO4 = - 3.71 m, log MoO4 = - 5.77 m, HFO = 0.267 g/L, I = 0.012 m)**

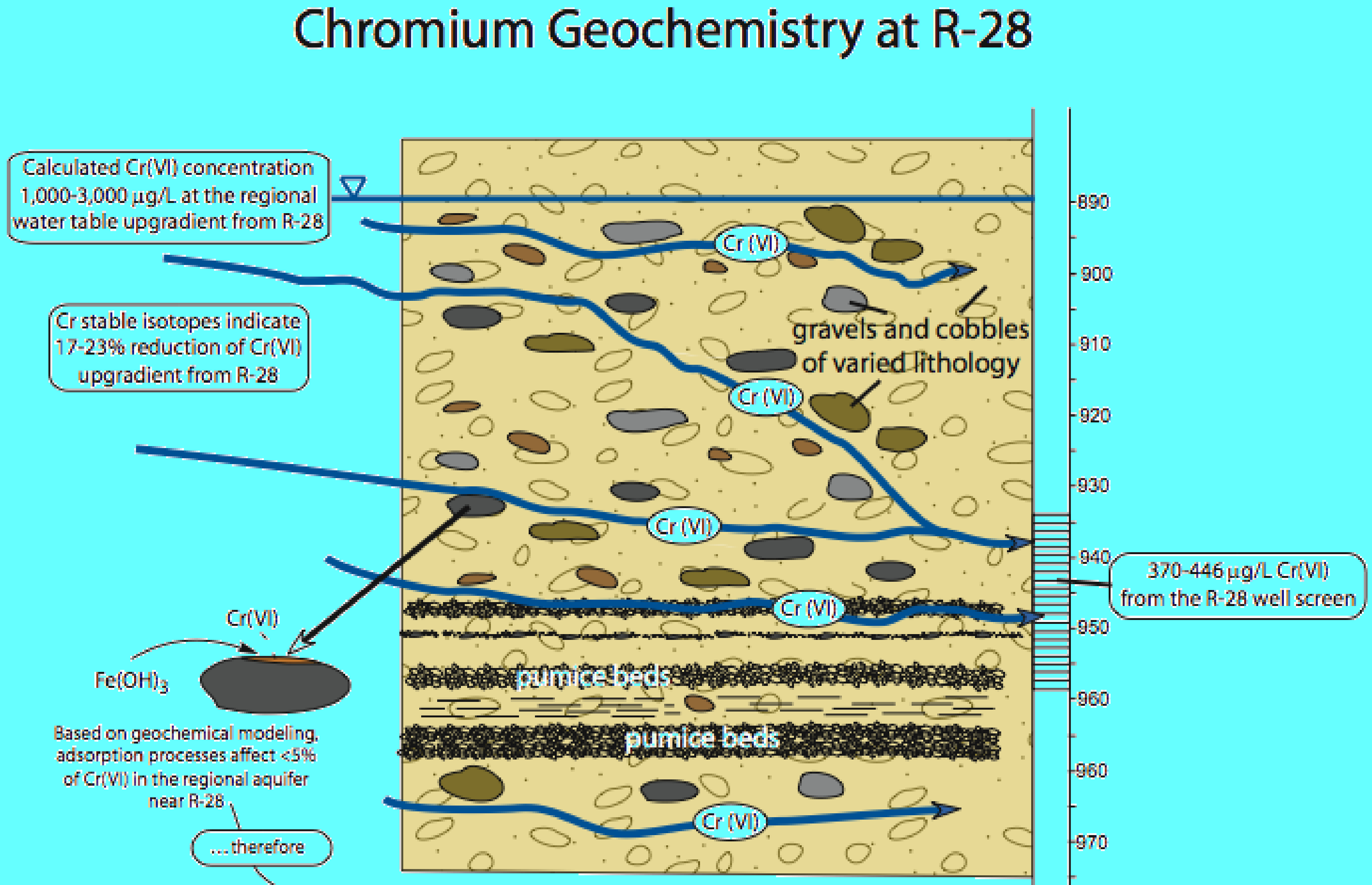



Calculated (MINTEQA2)Aqueous Species and Surfa
Complexes of Chromium(VI) Adsorbed onto Hydro
Ferric Oxide for SCC-2
100
90
80
70
60
50
40
30
20
10
0
5
6
7
8
9
pH
CrO4-2
HCrO4-
NaCrO4-
FeCrO4-(HD)
FeCrO4-(LD)
FeOHCrO4-2

# Distributions of Chromium in the Vadose Zone, Sandia Canyon



# Geochemical Conceptual Model for Chromium in Miocene Sediments, Mortandad Canyon



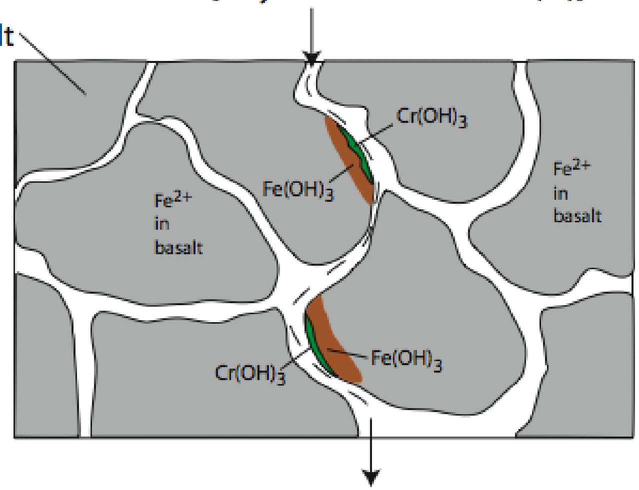

- Dilution and dispersion are probably the dominant physical processes controlling Cr(VI) concentrations within the regional aquifer.
- Chromium(VI) is not observed above background at downgradient wells.

# Geochemical Conceptual Model for Chromium in the Cerros del Rio Basalt

## Chromium Geochemistry within Cerros del Rio Basalt

Input Cr(VI) at higher concentrations
$\delta^{53}$Cr <1 ‰ [very little reduction of Cr(VI)]

Cerros del Rio basalt




$$3Fe^{2+} + CrO_4^{2-} + 8H_2O \longrightarrow Cr(OH)_3 + 3Fe(OH)_3 + 4H^+$$

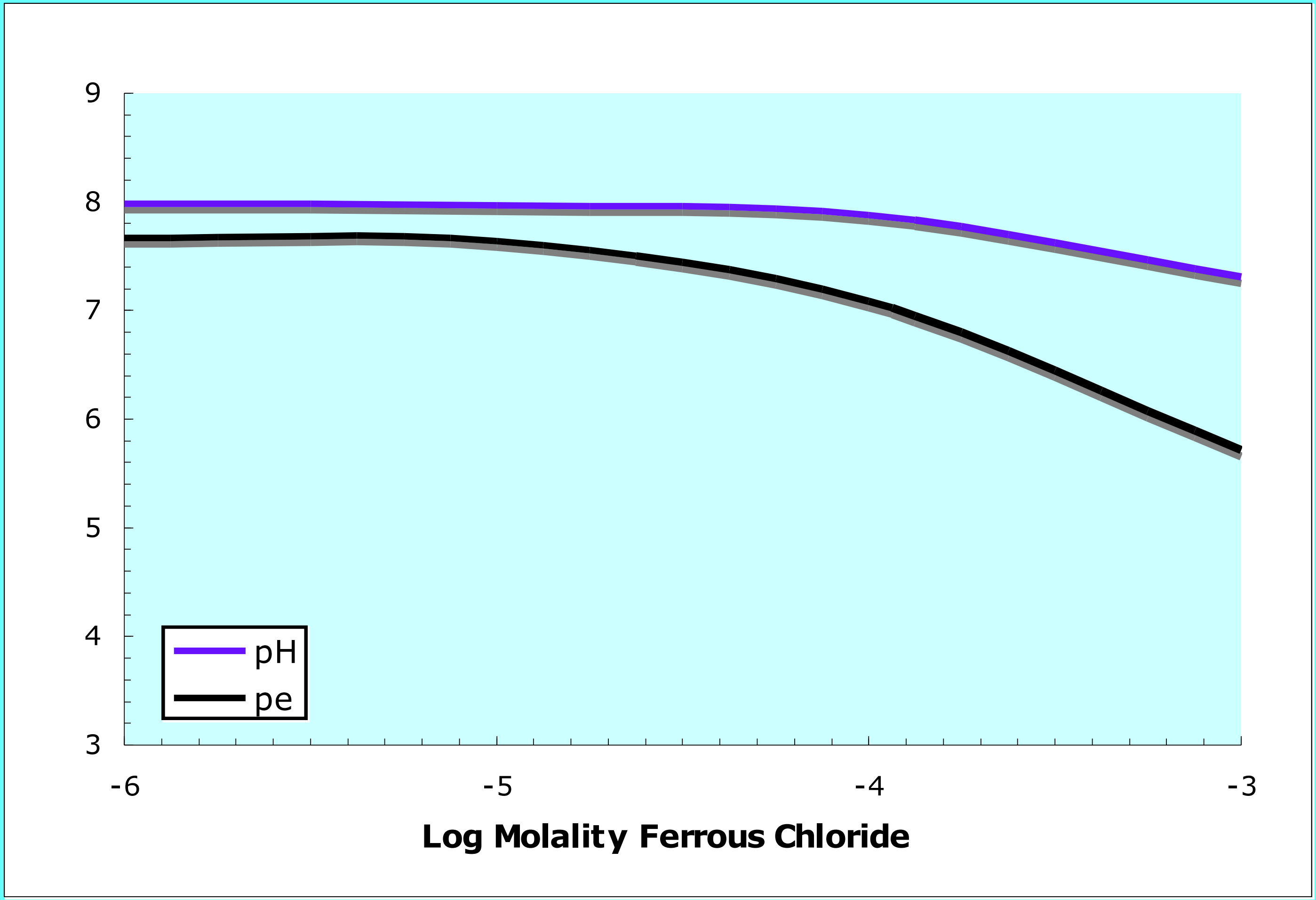
Reduction of Cr(VI) is followed by precipitation of Cr(III) [as $Cr(OH)_3$]

Output Cr(VI) at lower concentrations
$\delta^{53}$Cr up to 3 ‰ [significant reduction of Cr(VI)]

*Importance of Cerros del Rio basalt in transforming chromium(VI) to chromium(III):*

- Chromium(VI) is mobile in groundwater above pH 7
- Iron(II) concentrated in Cerros del Rio basalt chemically transforms Cr(VI) to Cr(III) as chromium hydroxide ($Cr(OH)_3$), which is much less soluble than Cr(VI)

# Results of Geochemical Modeling (PHREEQC2.2) Reacting R-28 Groundwater with Ferrous Chloride in Equilibrium with Calcite



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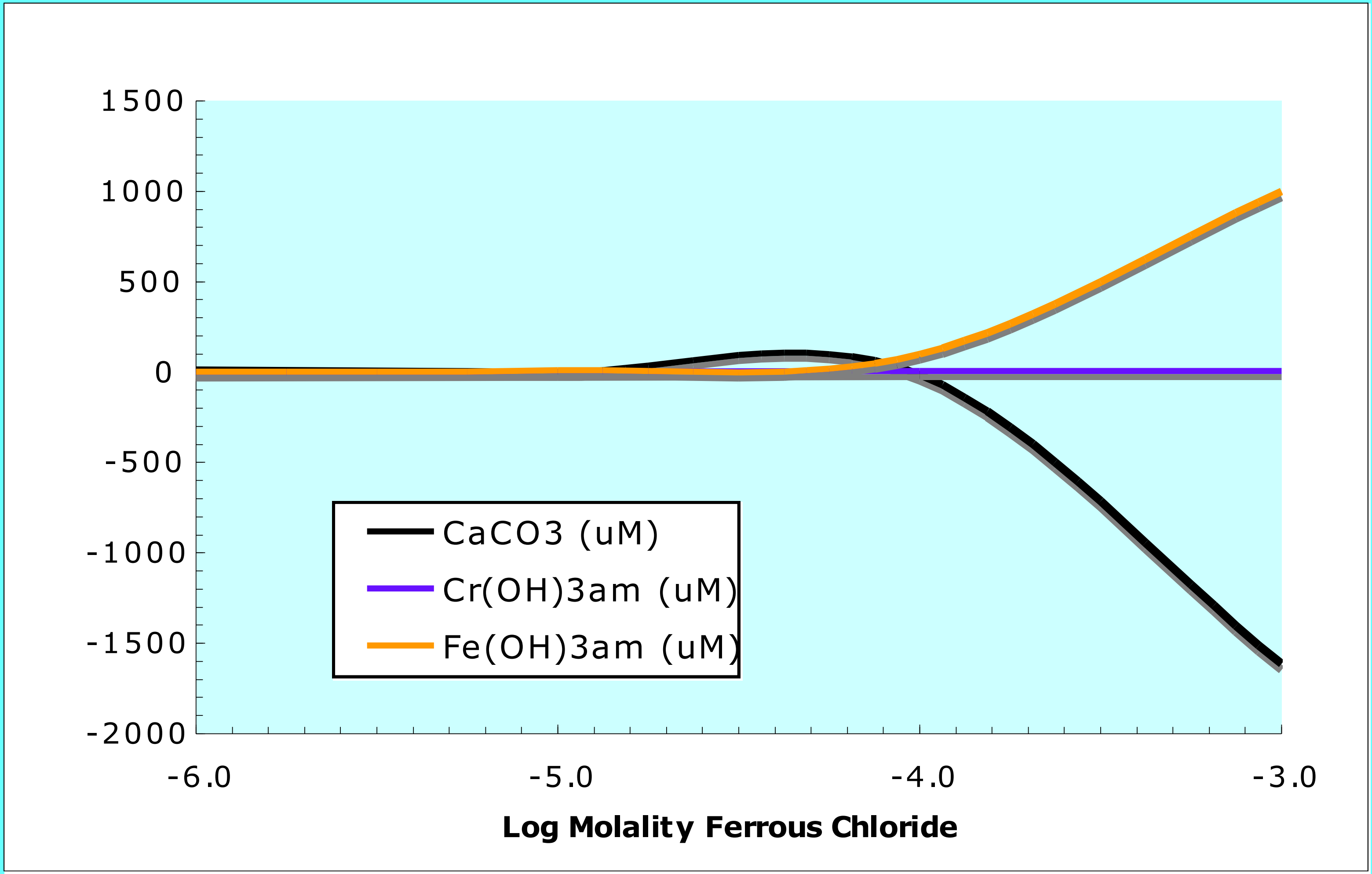


# Sources of Uranium

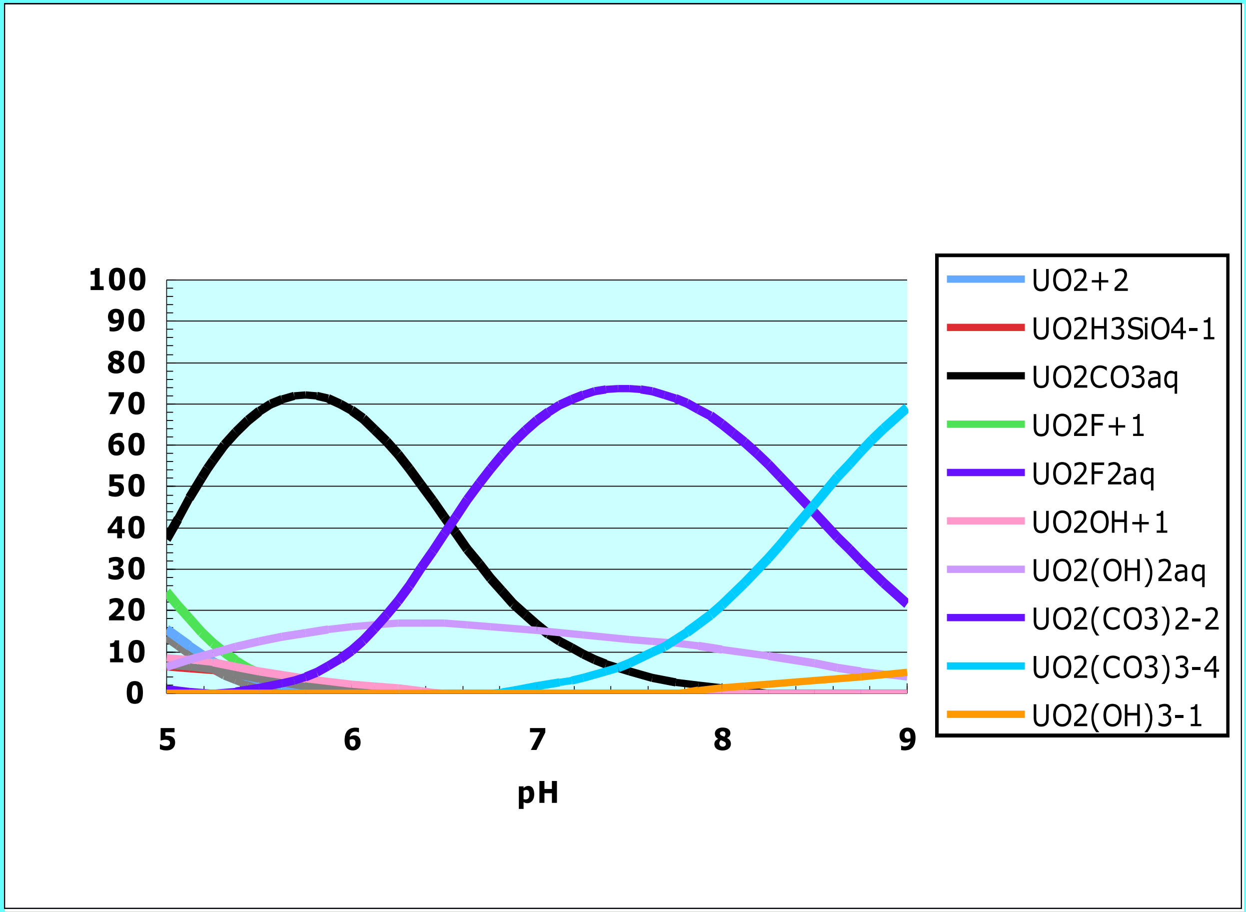
***Natural*** **-** Whole rock concentrations of uranium range from <1 mg/kg to >15 mg/kg.

Uranium-bearing solids, at pH 7, have varying solubilities in which silica glass ($10^{-2.71}$ M) is the most soluble and $ZrSiO_4$ ($10^{-15.54}$ M) is the least soluble.

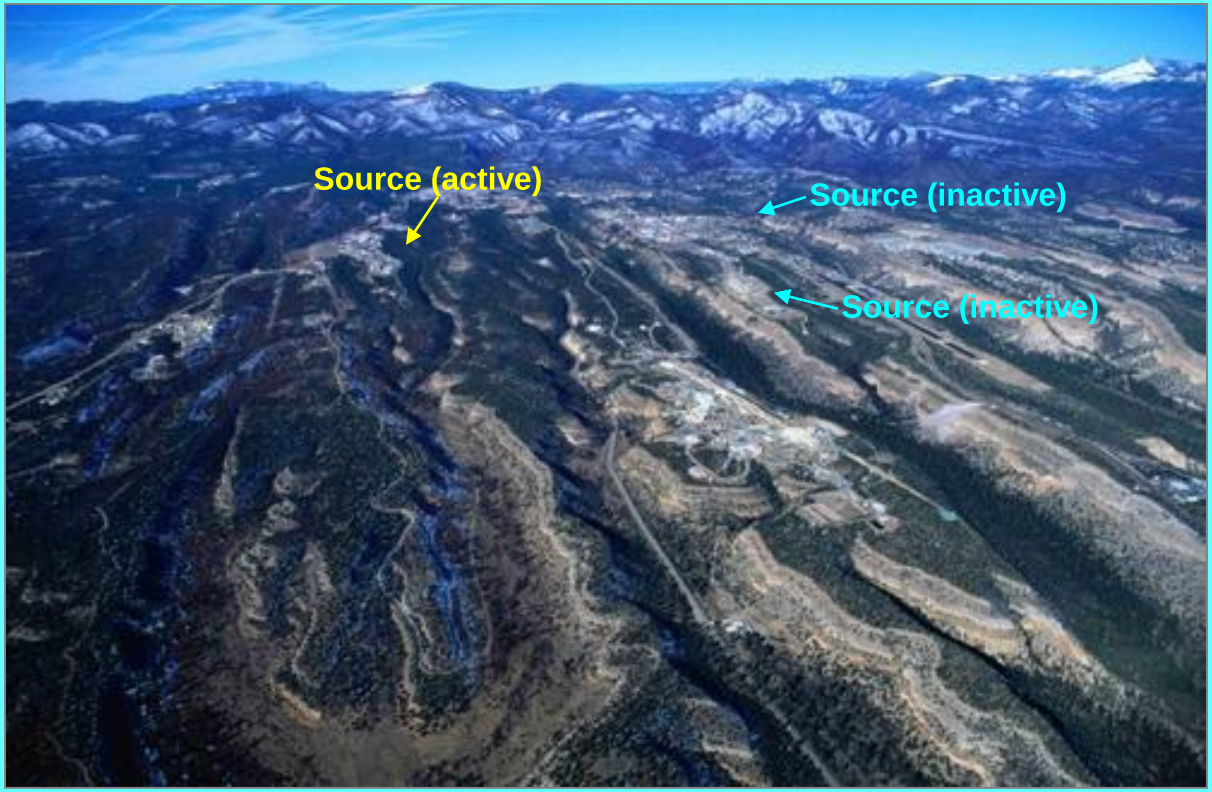
Natural uranium concentrations exceed $10^{-7.90}$ M (3.0 μg/L) east of the Rio Grande, within the Española Basin.

# Calculated Distribution of Dissolved U(VI) Species (MINTEQA2), Regional Aquifer (Median Composition), Los Alamos, New Mexico

**(log m U(VI) = -8.72, log m total $CO_3$ = -2.95 log m $H_4SiO_4$ = -2.94, and log m F = -4.77)**

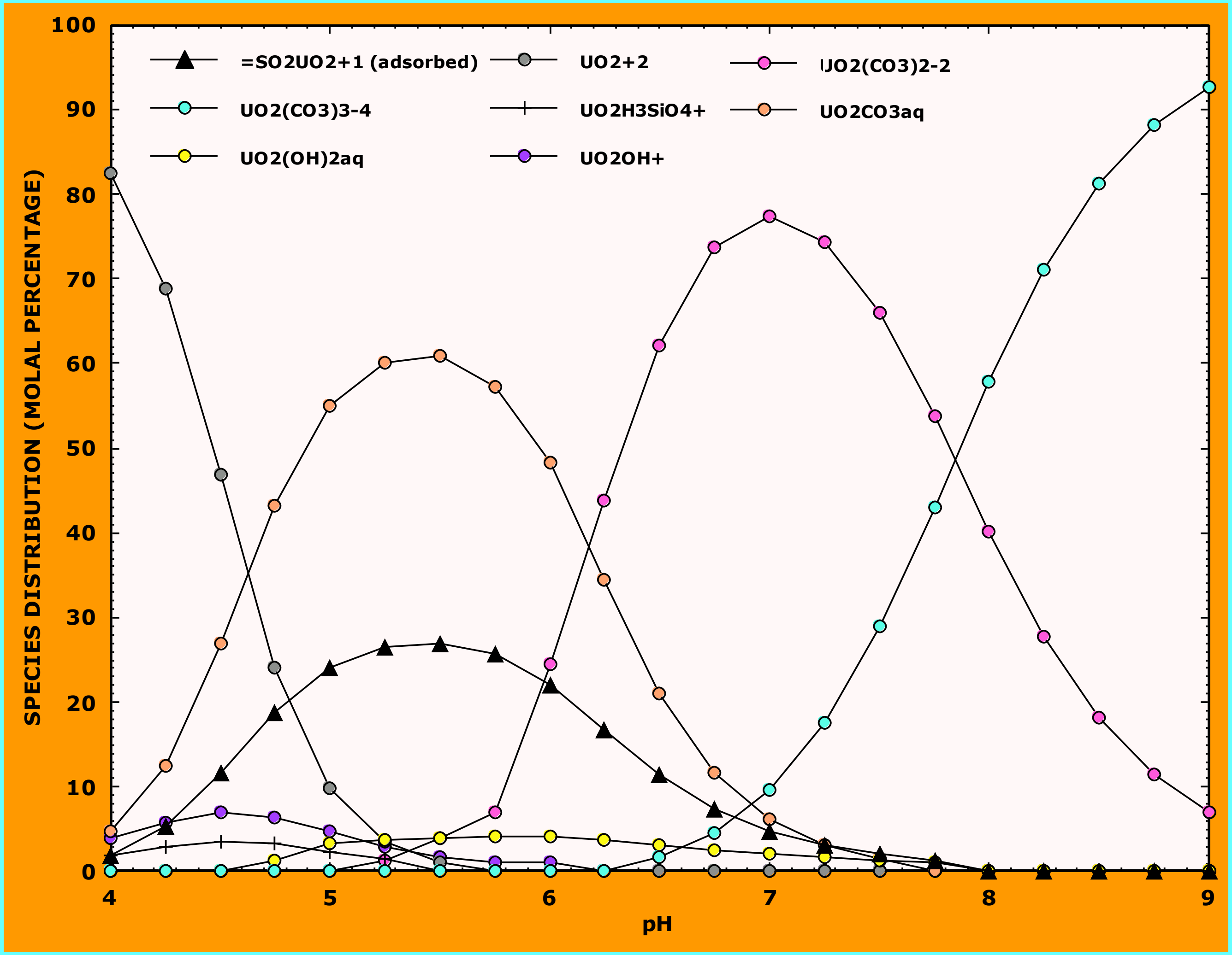


# Photograph of the Jemez Mountains and Pajarito Plateau
## (view to the west with industrial sources of uranium discharges)



# Surface Complexation Modeling (MINTEQA2) of U(VI) onto Hydrous Ferric Oxide (HFO), Spring 2B, White Rock Canyon, New Mexico

**(log [$UO_2^{2+}$] = -7.0, log [$H_4SiO_4$] = -2.90, log [total $CO_3^{2-}$] = -2.70, HFO = 0.009 g/L, I = 0.007 m)**



# Hydrochemical Conceptual Model for Part of the Española Basin, New Mexico