
Good Morning!

Hexavalent Chromium Contamination in Deep Groundwater Beneath Los Alamos National Laboratory, New Mexico

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(2012 EPA NARPM Training Program)

Outline

- What's the problem?
- Area of investigation
- Contaminant sources, history of releases, monitoring efforts, etc.
- Site-specific hydrogeology and contaminant transport
- The "Chromium Story", from the beginning
- Attenuation of Cr along the major flow paths, hydrochemistry, etc.

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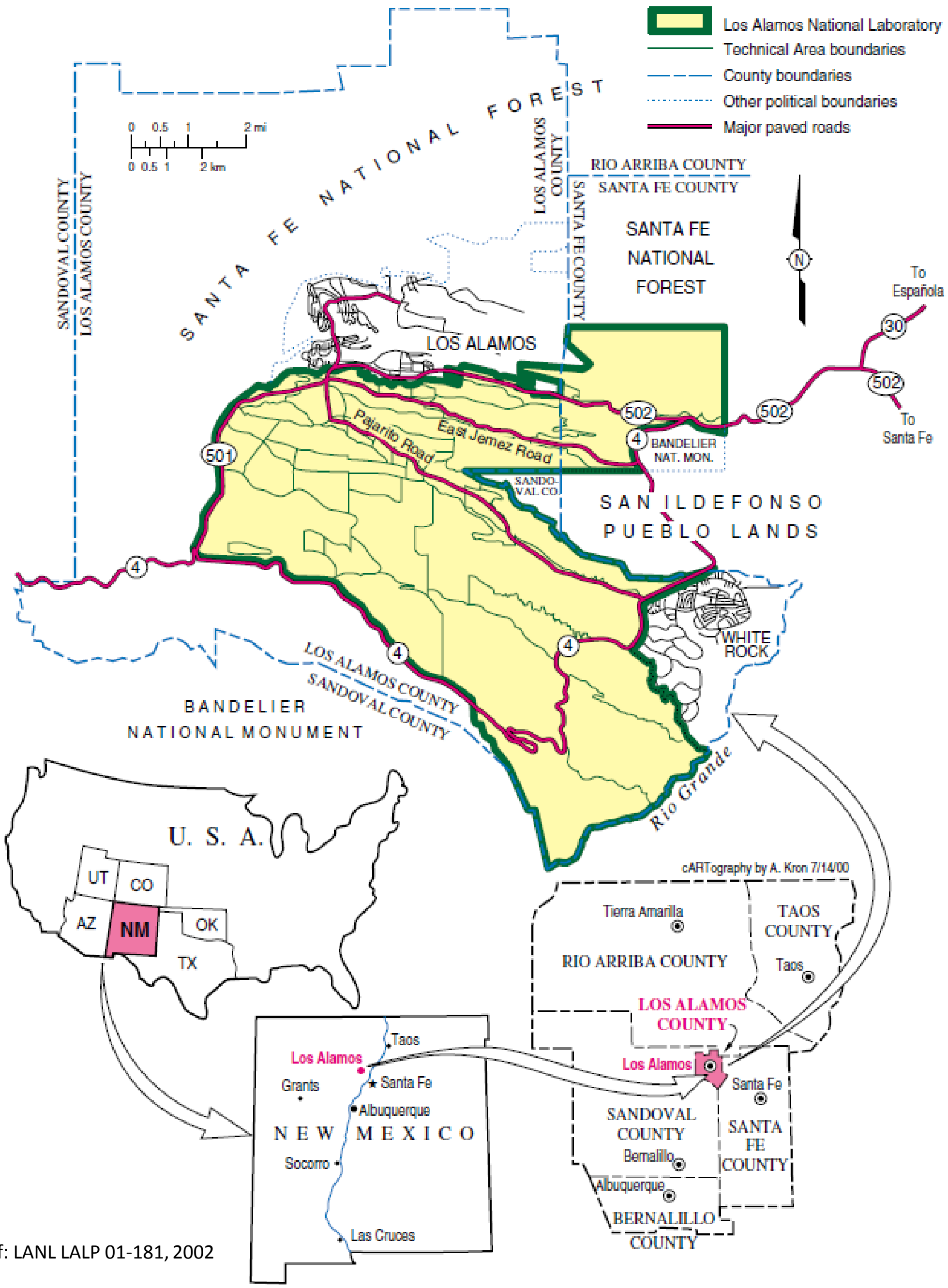

Ref: LANL LALP 01-181, 2002


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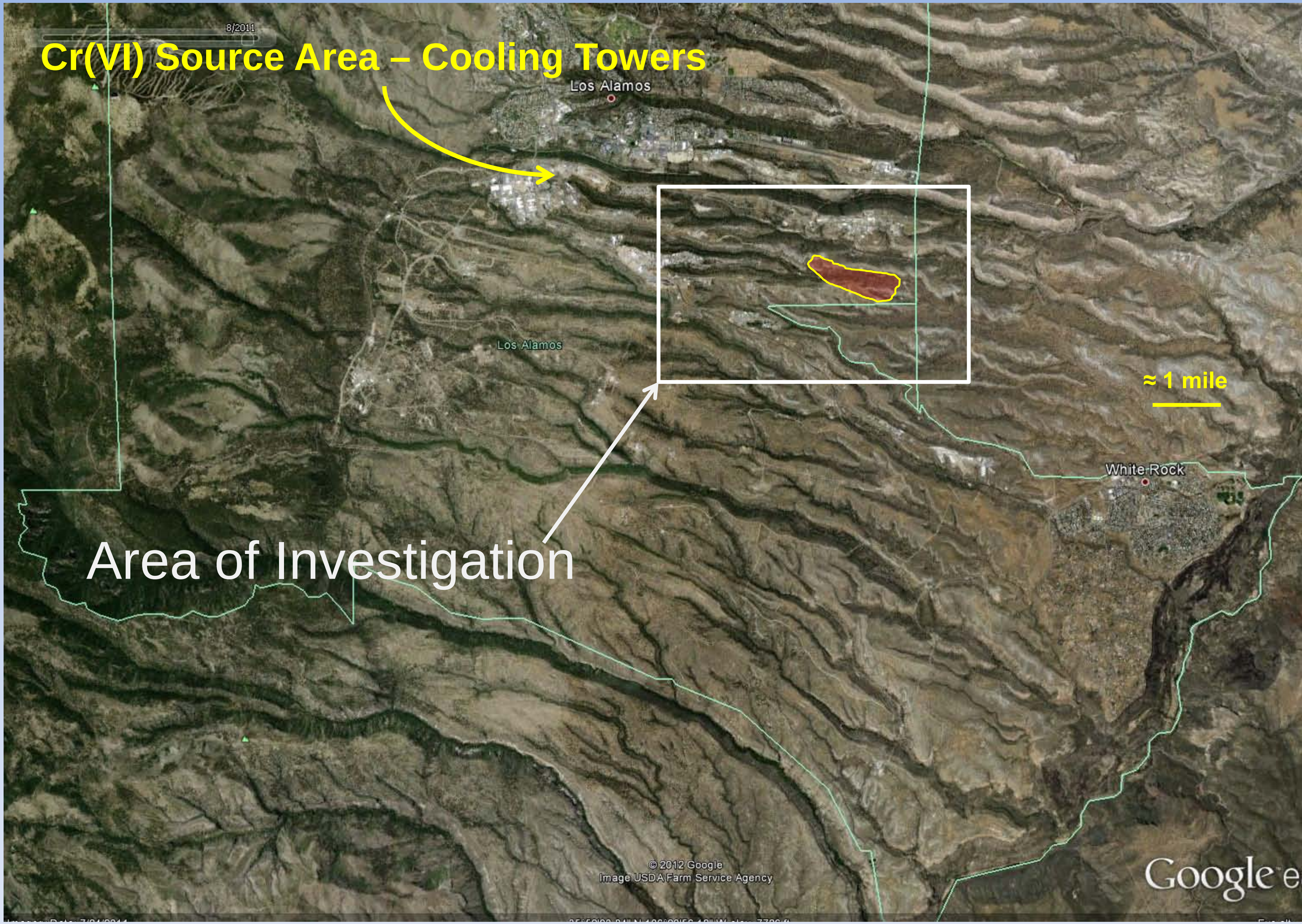
8/2011
Cr(VI) Source Area – Cooling Towers
Los Alamos
Los Alamos
Area of Investigation
≈ 1 mile
White Rock
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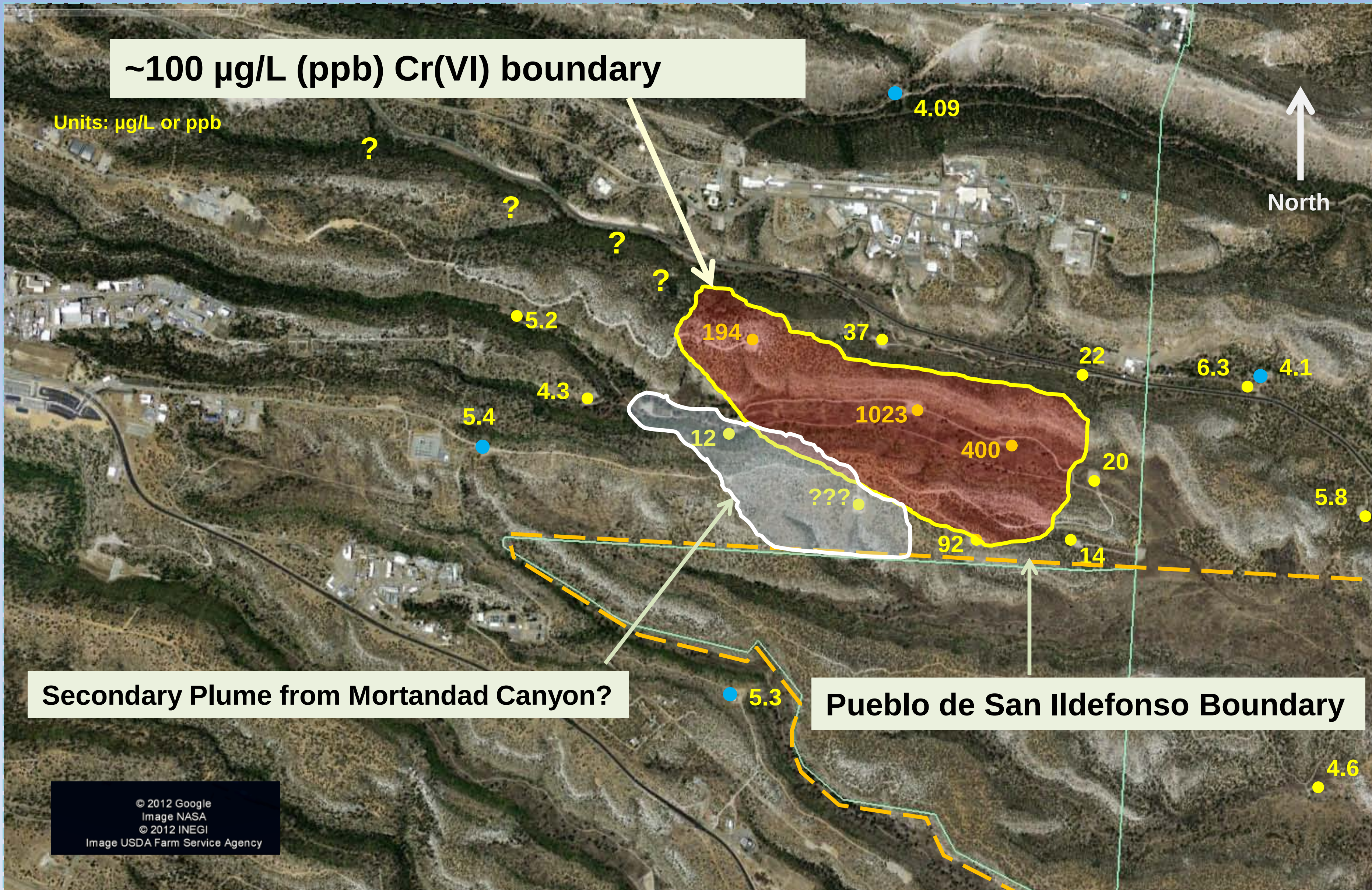
Image USDA Farm Service Agency

Hexavalent Chromium Plume

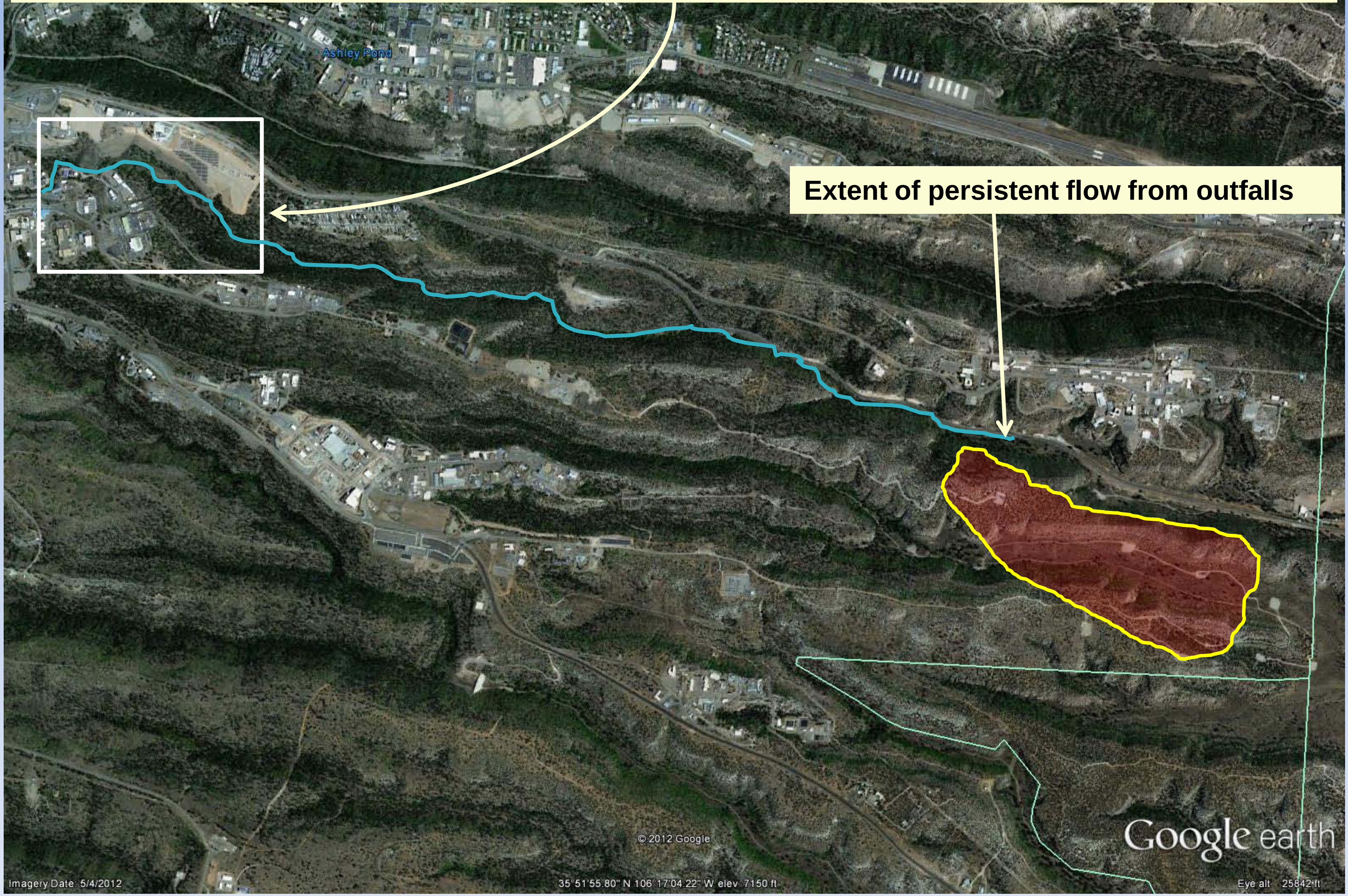


0.5 Mile

Drinking-Water Production Well

Monitoring Well

Cr(VI) as CrO_4^{2-} Discharge Source Area - Sandia Wetland




3/25/2006
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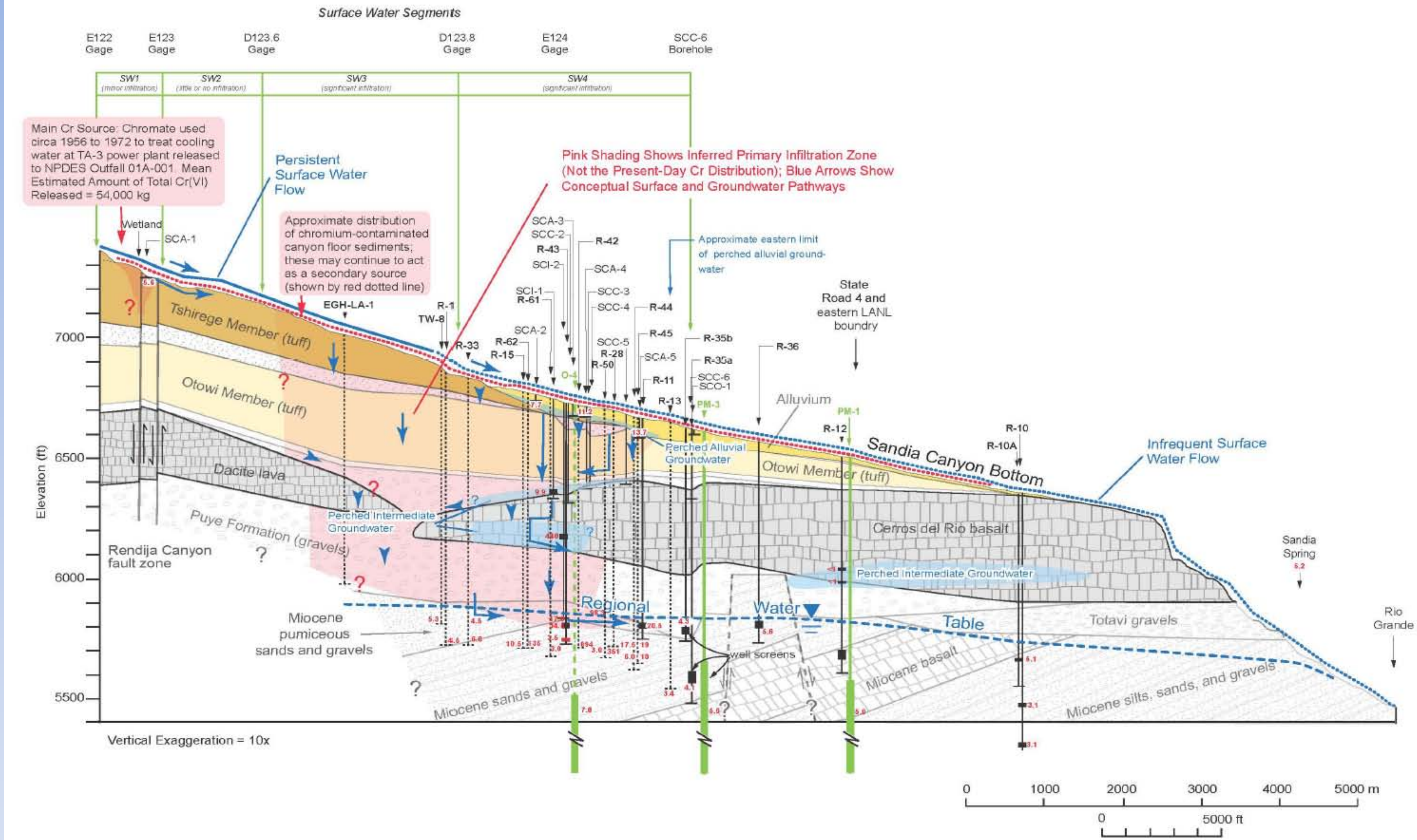
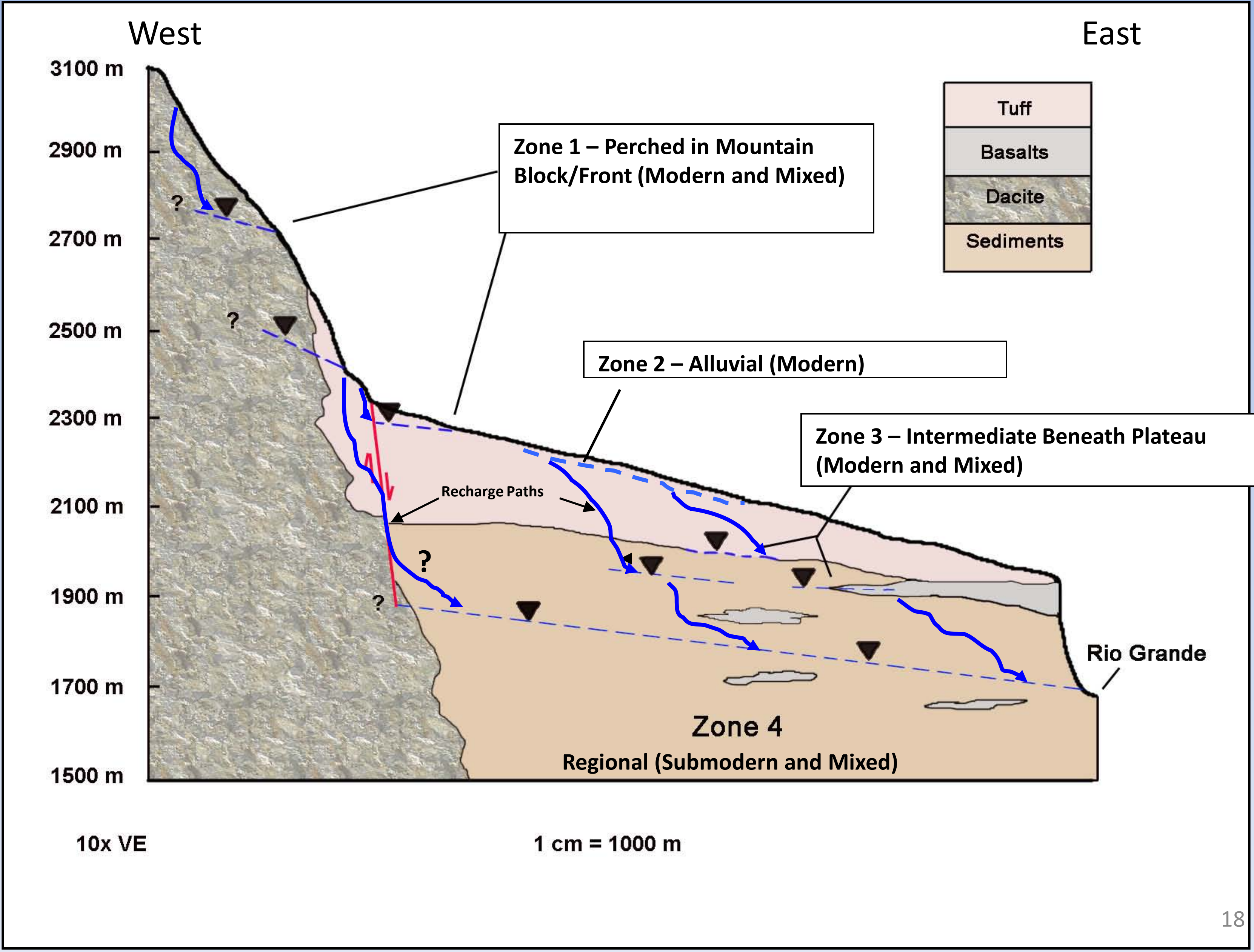
CrO_4^{2-} Source: Cooling Towers Head of Sandia Wetland



Source: LANL, LA-UR-12-24593, EP2012-0195

Generalized Cross Section Showing Ground-water Type and Expected Trends in Ground-water Age for Conceptual Model of Ground-water Flow



The "Chromium Story"

- Cr(VI) contamination was "accidently" identified in 2004 at Well R-28
- Four years earlier, a borehole was drilled about 100' west of R-28 to a depth of 950' bgs or within about 150' of the regional aquifer water table; after reaching total depth the borehole was plugged and abandoned
- At R-28, the first sampling event in January 2004 showed Cr at about 400 µg/L but was not reported to the State until December 2005
- After the initial discovery of Cr(VI), the facility (LANL) installed nine (9) new monitoring wells during the period 2005 and 2011 in order to delineate the nature and extent of chromium contamination
- Regulatory deliverables related to chromium contamination:

1) Work Plan for Sandia Canyon and Cañada del Buey, 1999 (LA-UR-99-3610)

2) Interim Measures Work Plan for Chromium Contamination in Groundwater, 2006 (EP2006-0214)

3) Interim Measures Investigation Report for Chromium in Groundwater, 2006 (EP2006-1039)

4) Fate and Transport Investigations Update for Chromium Contamination from Sandia Canyon, 2008 (EP2008-0374)

5) Investigation Report for Sandia Canyon, 2009 (EP2009-0516) …………………cont., next slide

5) Phase II Investigation Work Plan for Sandia Canyon, 2010 (EP2010-0290)

6) Phase II Investigation Report for Sandia Canyon, 2012 (EP2012-0195)

So, what's next?

- **Another IM or pilot pump and treat?**
- **Begin the CME process?**
- **????**

Redox Behavior of Chromium in Aqueous Environments

The redox transformation of Cr(III) to Cr(VI) or vice versa can only take place in the presence of another redox couple which accepts or donates three necessary electrons.

Cr Oxidation:

Manganese oxides are likely to be responsible for most Cr(III) oxidation in aqueous systems.

$Cr(OH)_3(am) + 1.5MnO_2(s) + H^+ = CrO_4^{2-} + 1.5Mn^{2+} + 2H_2O$

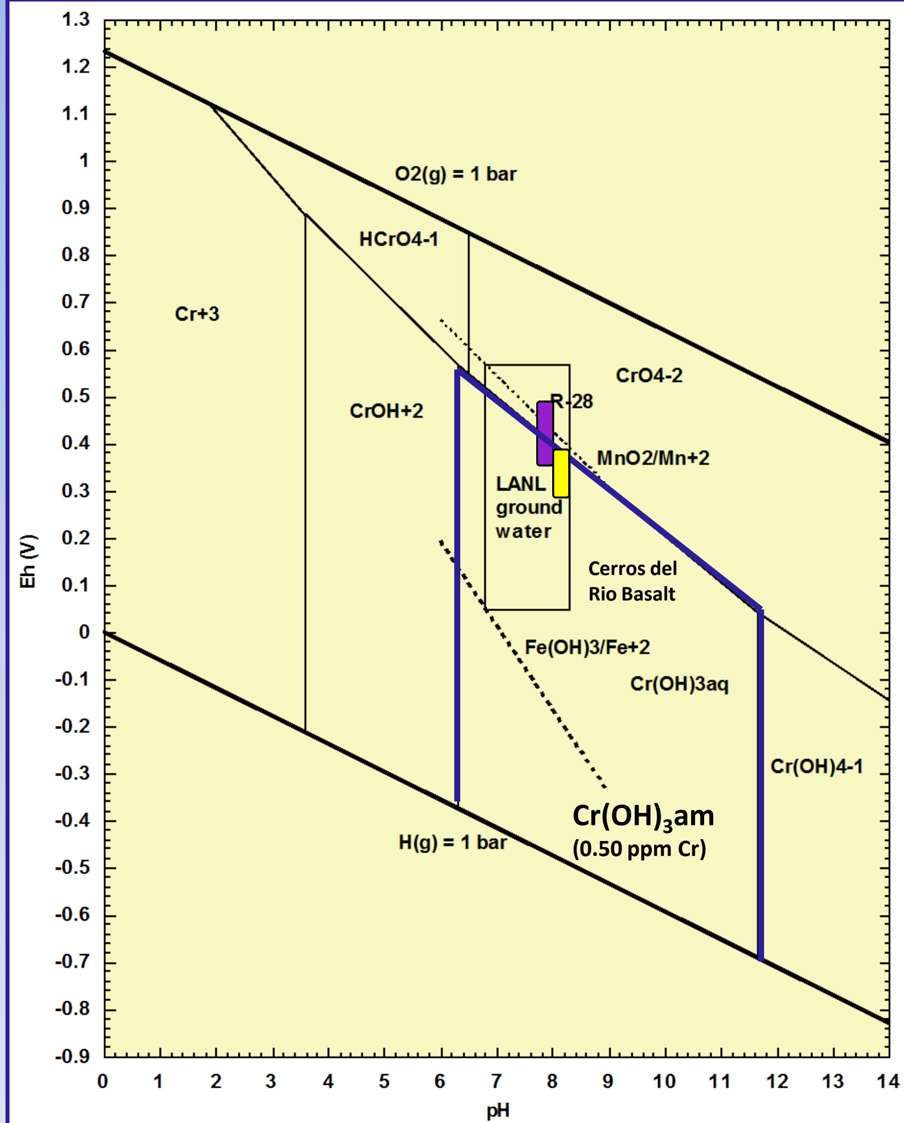
$Cr(OH)_3(am) + 3MnO_2(s) + H_2O = CrO_4^{2-} + 3MnOOH(s) + 2H^+$

Cr Reduction:

Weathering of Fe(II)-containing minerals (biotite, hematite, some clays, etc.)

Dissolved Fe(II) and organic carbon

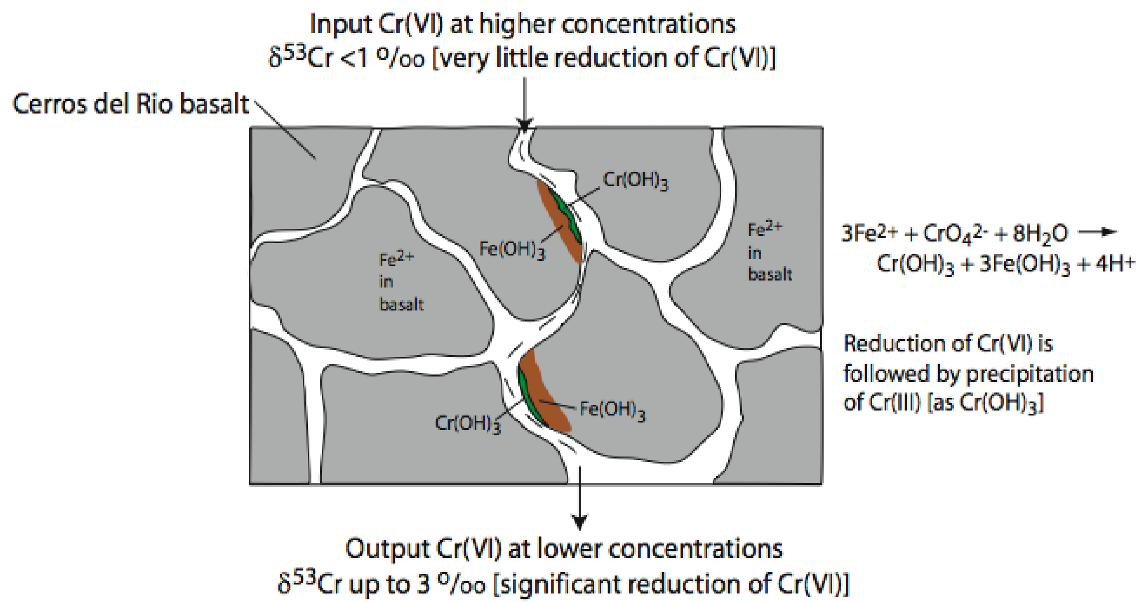
Solid organic matter



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.

Geochemical Conceptual Model for Chromium in the Cerros del Rio Basalt

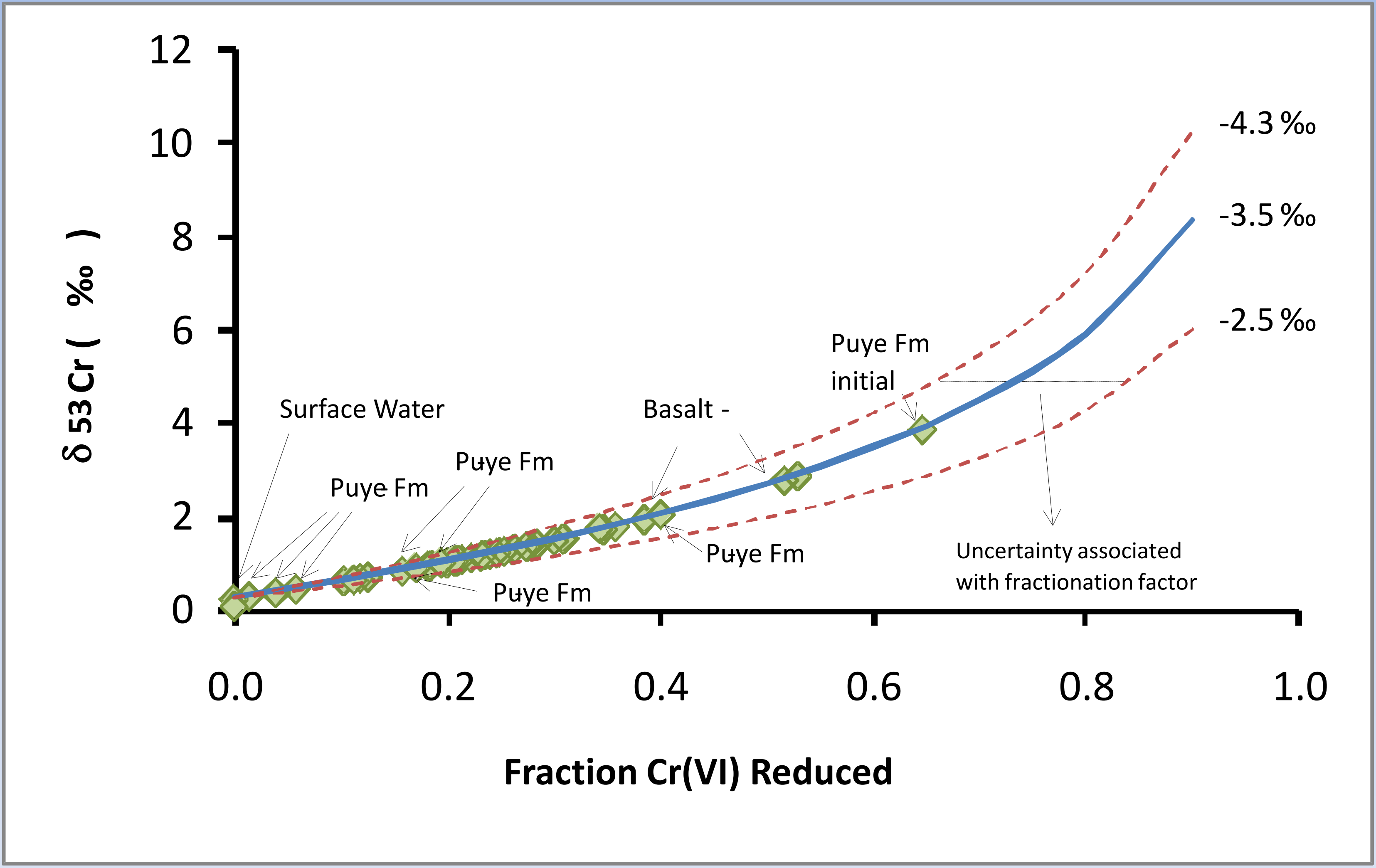
Chromium Geochemistry within Cerros del Rio Basalt



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

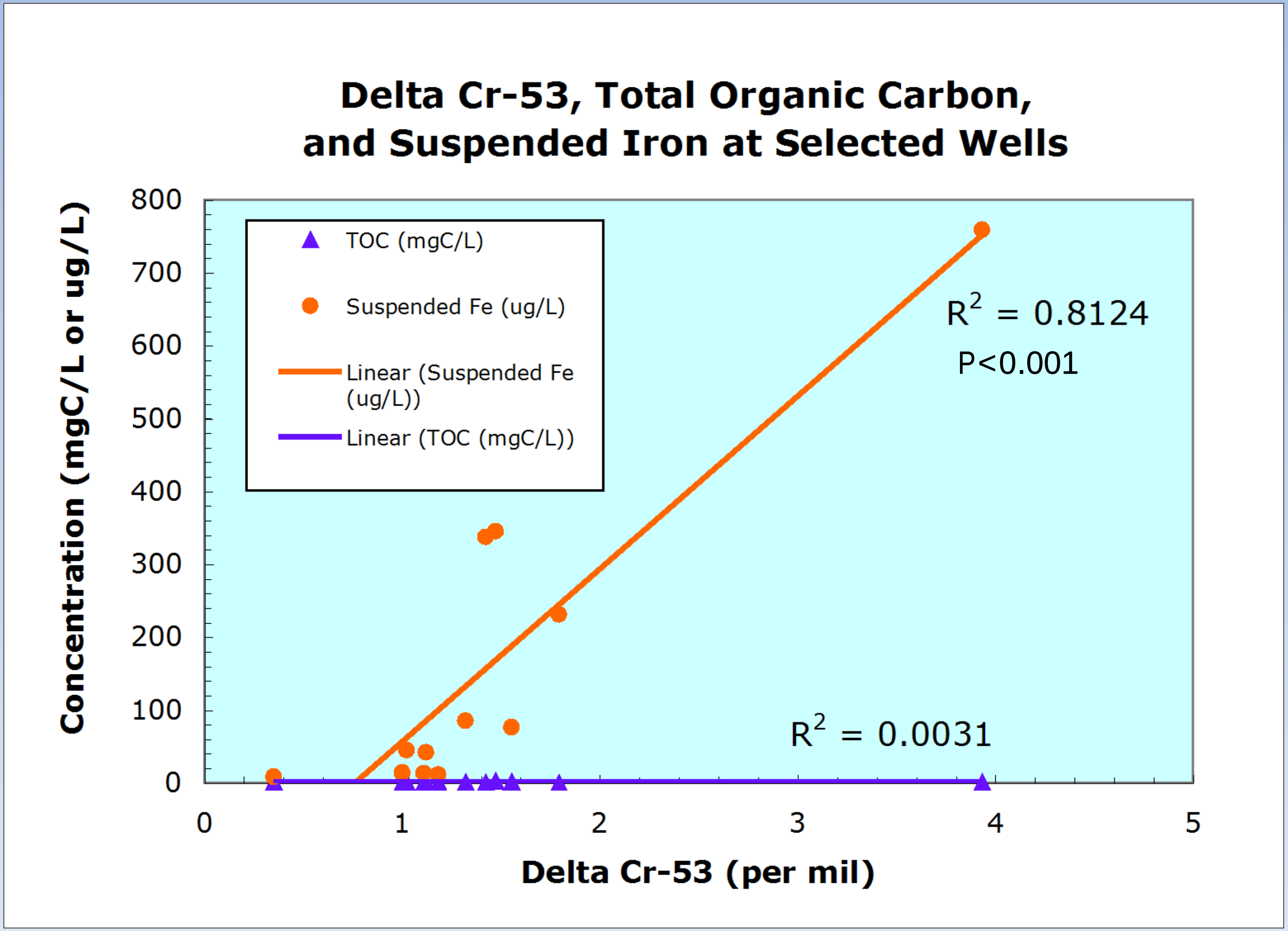
- Chromium(VI) is mobile in groundwater above pH 7
- Iron(II) concentrated in Cerros del Rio basalt chemically transforms Cr(VI) to Cr(III) as chromium hydroxide ($Cr(OH)_3$), which is much less soluble than Cr(VI)

Fraction of Chromium(VI) Reduced Versus $\delta^{53}Cr$ Ratios in Groundwater, Los Alamos, New Mexico



Source: Heikoop and Longmire, 2009

δ^{53}Cr Ratios Versus Total Organic Carbon and Suspended Iron, Los Alamos, New Mexico



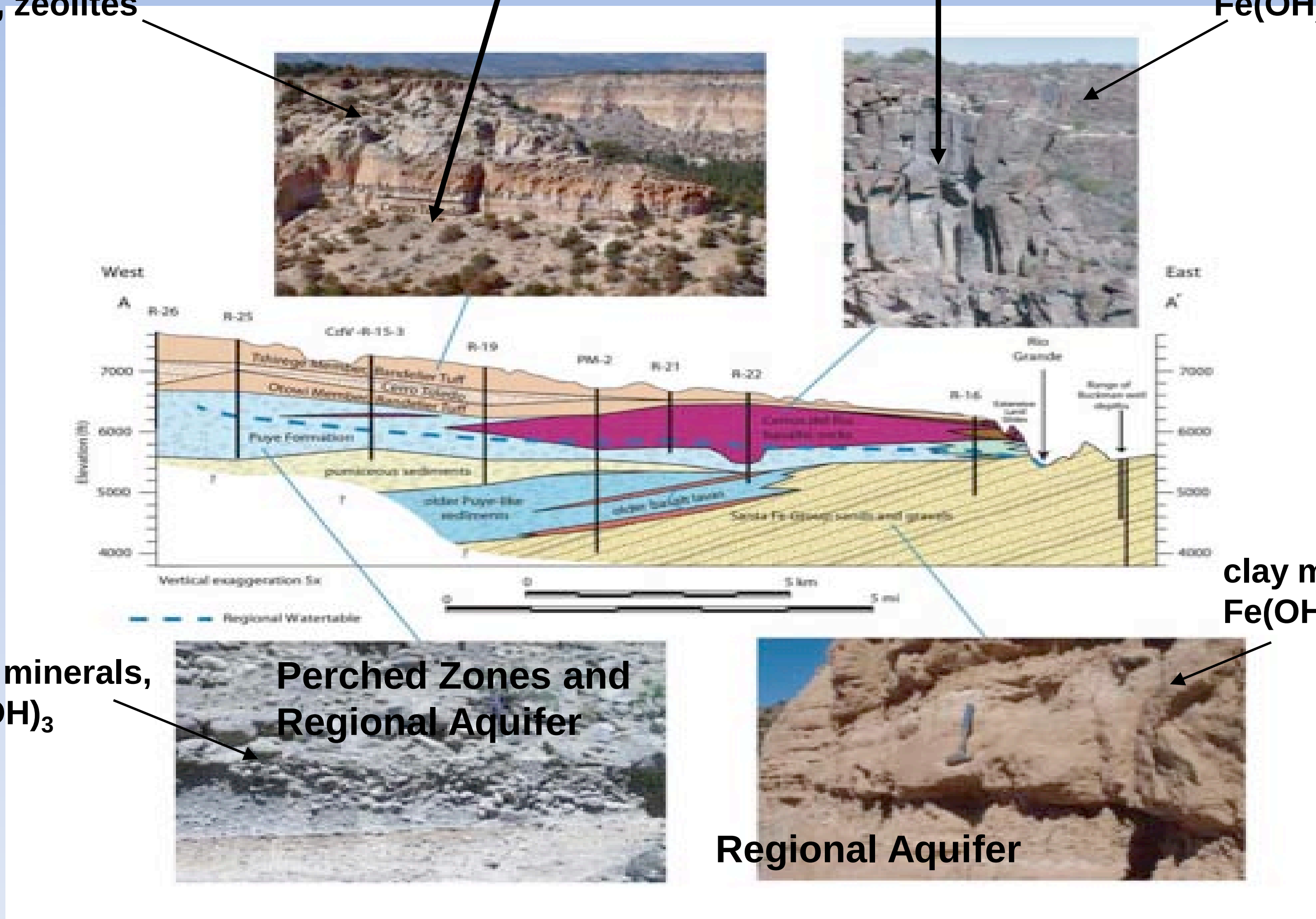
LANL Hydrostratigraphy and Reactive Solids

clay minerals, $Fe(OH)_3$, zeolites

Perched Zones

Perched Zones and Regional Aquifer

clay minerals, $Fe(OH)_3$, calcite



clay minerals, $Fe(OH)_3$, calcite

clay minerals, $Fe(OH)_3$

Perched Zones and Regional Aquifer

Regional Aquifer

Redox Behavior of Chromium in Aqueous Environments

Hydroquinone Dissociation

$C_6H_6O_2 = C_6H_5O_2^- + H^+$

$C_6H_5O_2^- = C_6H_4O_2^{2-} + H^+$

Hydroquinone Oxidation

$C_6H_6O_2 = C_6H_4O_2 + 2H^+ + 2e^-$

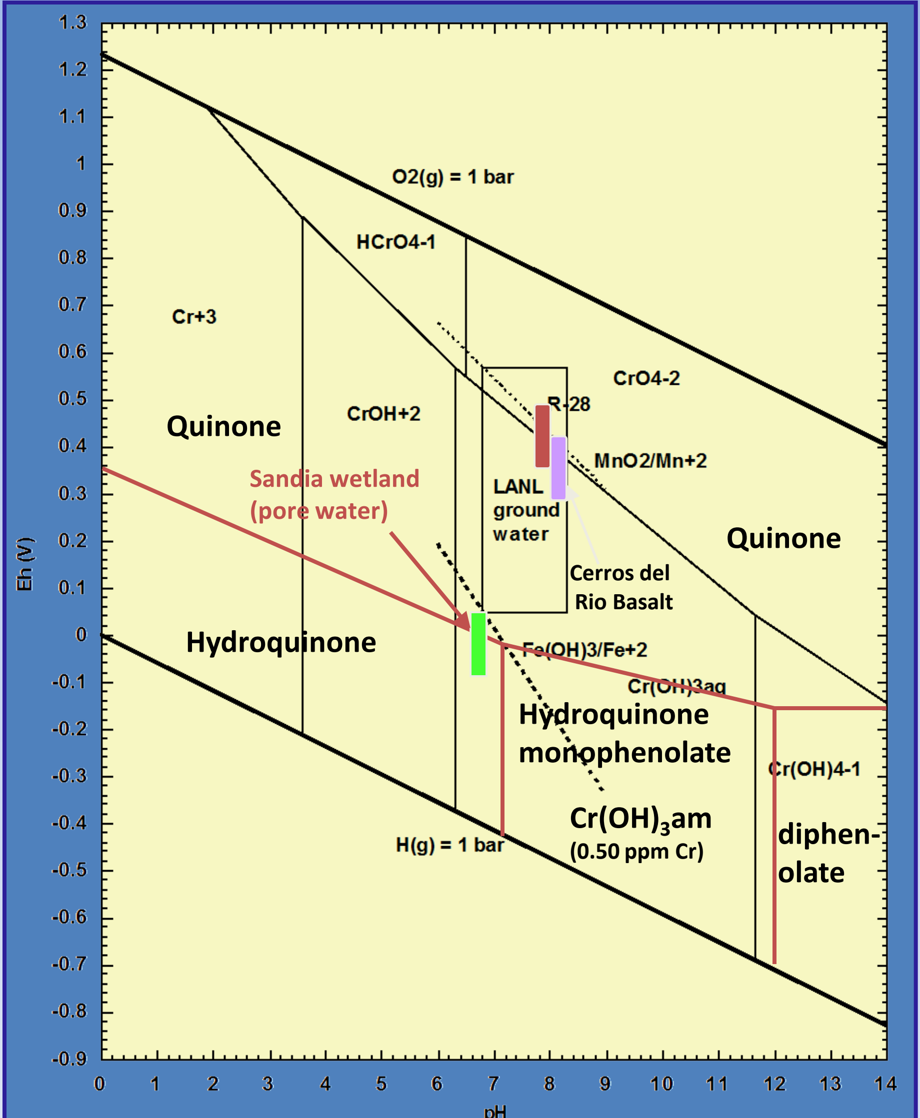
Cr Reduction:

$CrO_4^{2-} + 1.5C_6H_6O_2 + 2H^+$

$= Cr(OH)_3(am) + 1.5C_6H_4O_2 + H_2O$

General references: Stevenson, F. J., 1994, Humus Chemistry: Genesis, Composition, Reactions: Wiley, New York, 496 p.

McBride, M.B., 1994, Environmental Chemistry of Soils: Oxford University Press, New York, 406 p.



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.

Chromium Reduction Capacity of Sandia Canyon Wetland (Saturated), Los Alamos, New Mexico

Parameter	Sample 07-236a	Sample 07-236b	Sample 07-92a	Sample 07-92b
Total Cr (mg/kg)	114	36.5	3580	18.5
Cr(VI) (mg/kg)	0.07	0.07	2.01	0.28
Total Fe (mg/kg)	6380	6560	5970	970
Fe(II) (mg/kg)	6360	6540	2660	230
Mn(IV) (mg/kg)	170	94.8	294	18.9
moles Fe(II)/g soil / moles Cr(VI)/g soil [$\geq$3]	8.46e+04	8.70e+04	1.23e+03	7.65e+02
Potential for Cr(III) to remain reduced based on Fe(II)/Cr(VI) mole ratio	Good	Good	Good	Good
moles Fe(II)/g soil / moles Mn(IV)/g soil [$\geq$1]	36.9	67.9	8.9	12.0
Potential for Cr(III) to remain reduced based on Fe(II)/Mn(IV) mole ratio	Good	Good	Good	Good

(LANL 2009, LA-UR-09-6450)

Remediation Options for Chromium in Soil and Aquifer Systems

Physical	Ion Exchange-Adsorption	Chemical Reduction-Precipitation
Pump and Treat [Cr(VI)]	Anion, Cr(VI): $HCrO_4^-$, CrO_4^{2-}, $Cr_2O_7^{2-}$, $Cr(OH)_4^-$	CaS_5, HRC, Fe(0), wetlands, humic and fulvic acids, microbial, $Na_2S_2O_4$, $NaHSO_3$, $CaHSO_3$, Na_2S, Fe(II), GAC, electrolysis, phytoremediation, ISV, electrokinetics
Membrane filtration	Cation, Cr(III): Cr^{3+}, $CrOH^{2+}$, $Cr(OH)_2^+$	
In-situ soil flushing		

Note: calcium polysulfide (CaS_5), HRC means hydrogen releasing compound, zero valence iron [Fe(0)], sodium dithionite ($Na_2S_2O_4$), sodium metabisulfite ($NaHSO_3$), calcium metabisulfite ($CaHSO_3$), GAC means granular activated carbon, and ISV means in-situ vitrification.

Summary and Conclusions for Sandia Canyon

- **Cr(VI) releases from cooling towers during the period 1956 to 1972 have migrated to the regional drinking-water aquifer with concentrations exceeding EPA's MCL by about 10 times.**

- **The spatial distribution of Cr(VI) in the regional aquifer suggests that: 1) the plume(s) is migrating along multiple flow paths or preferential flow paths; 2) nearby production-well pumping may induce transient behavior of the plume; and 3) along the plume front, Cr(VI) is moving deeper into the regional aquifer.**

- **Hydrochemical data collected from a recently completed well located upgradient of the main Cr(VI) plume suggest that multiple zones of infiltration may occur.**

- **The potential overlap or mixing of a secondary plume from Mortandad Canyon with the Sandia Canyon Cr(VI) plume complicates the conceptual model for contaminant transport .**

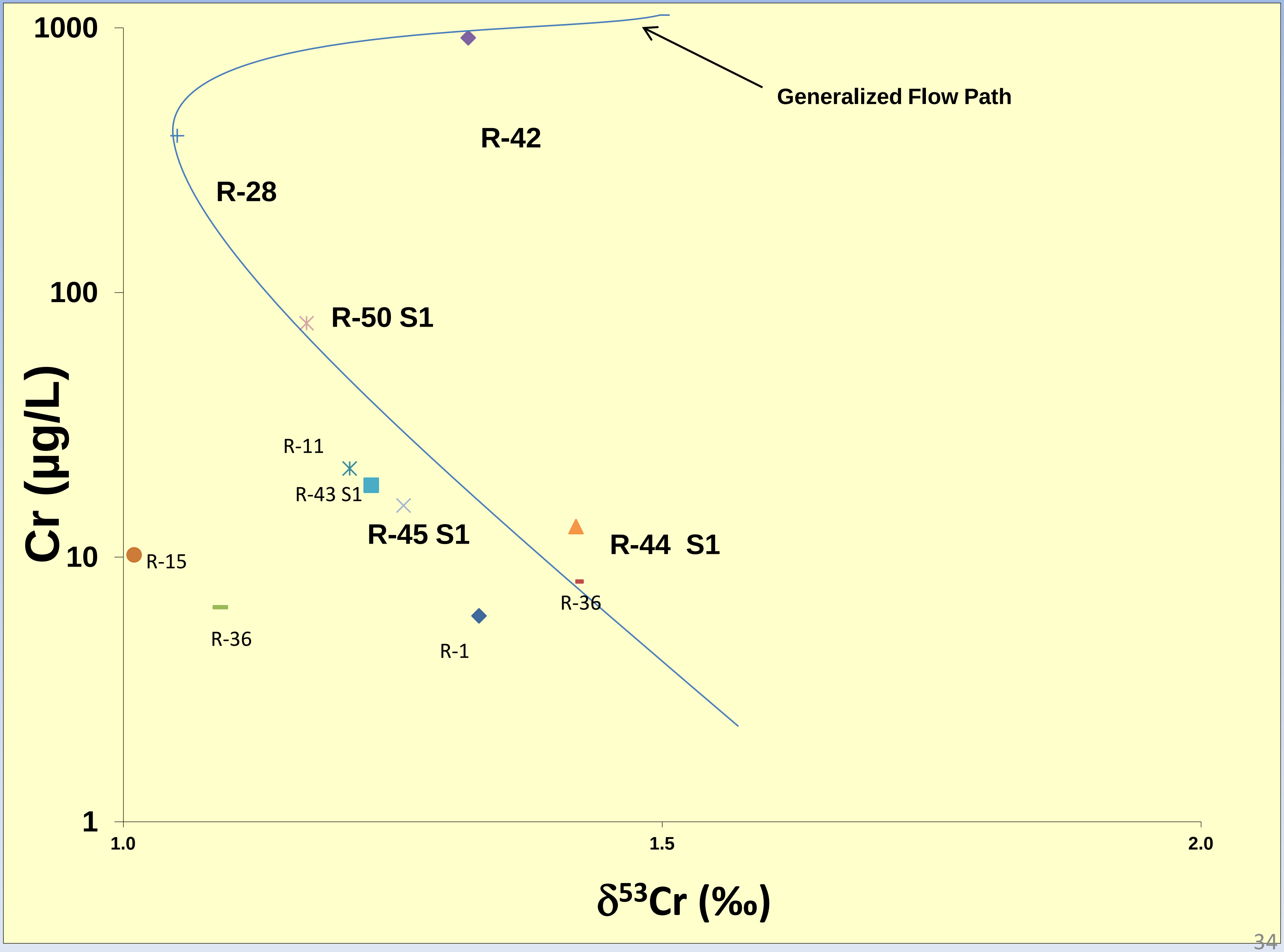
Summary and Conclusions for Sandia Canyon

- The Sandia Canyon wetland contains >97 percent Cr(III) of 11,000 kg Cr (median) with a range of 5700 to 27,000 kg Cr. Up to 49 percent of total Cr released is stored in the wetland.
- Molar ratios of Fe(II)/Cr(VI) and Fe(II)/Mn(IV) in Sandia wetland samples confirm stability of Cr(III) under current conditions.
- Chromium(VI) stable as CrO_4^{2-} under oxidizing and basic pH conditions characteristic of the regional aquifer.
- Stable isotopes of Cr are a useful tool along with ground water and aquifer material chemistry for quantifying mobility of Cr.


Questions?

Supplemental Material

Attenuation of Cr(VI) Along Flow Paths



Data Source: LANL EP2012-0195