HYDROCHEMISTRY OF CHROMIUM, LOS ALAMOS NATIONAL LABORATORY

BY

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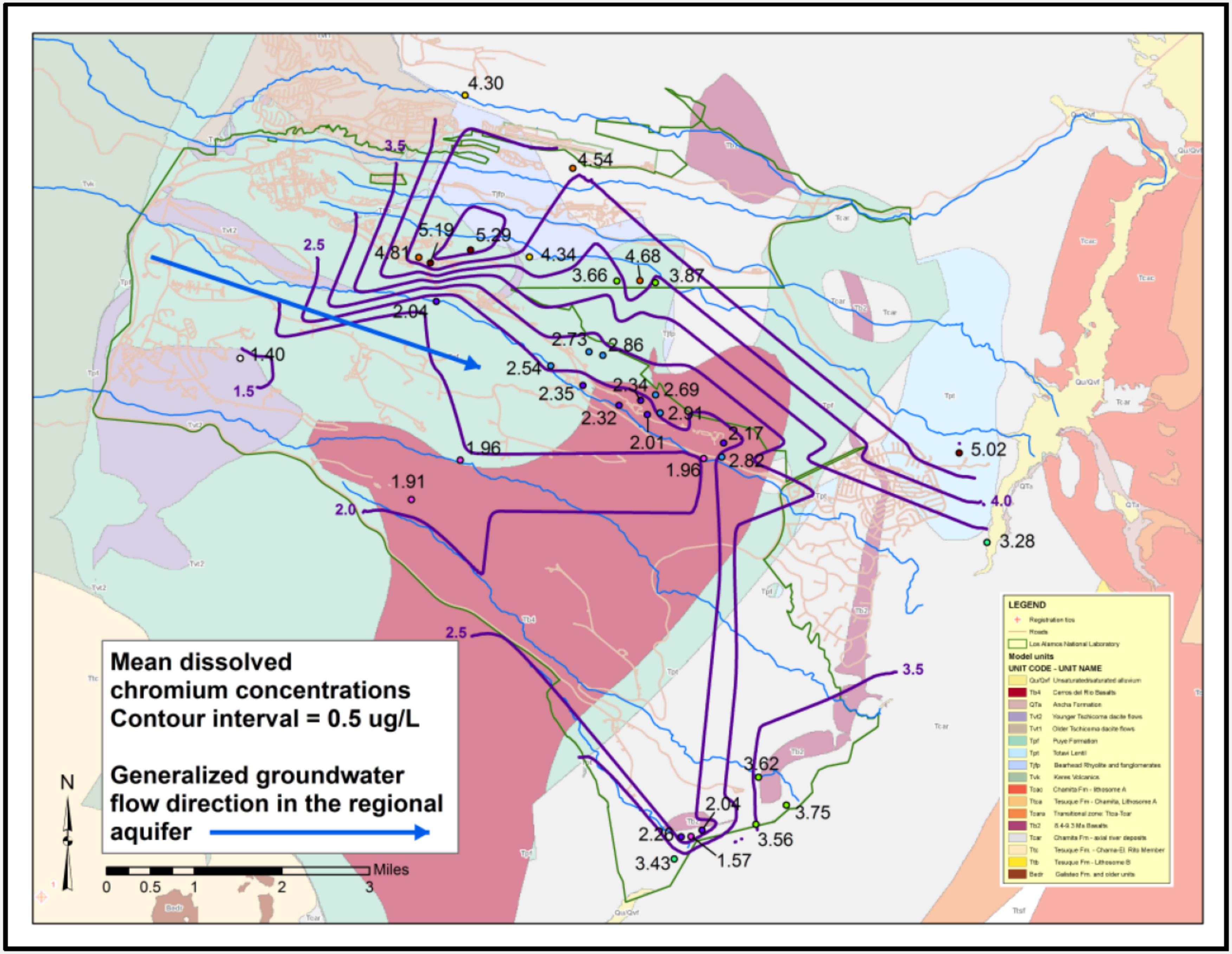
I. Sources of Chromium

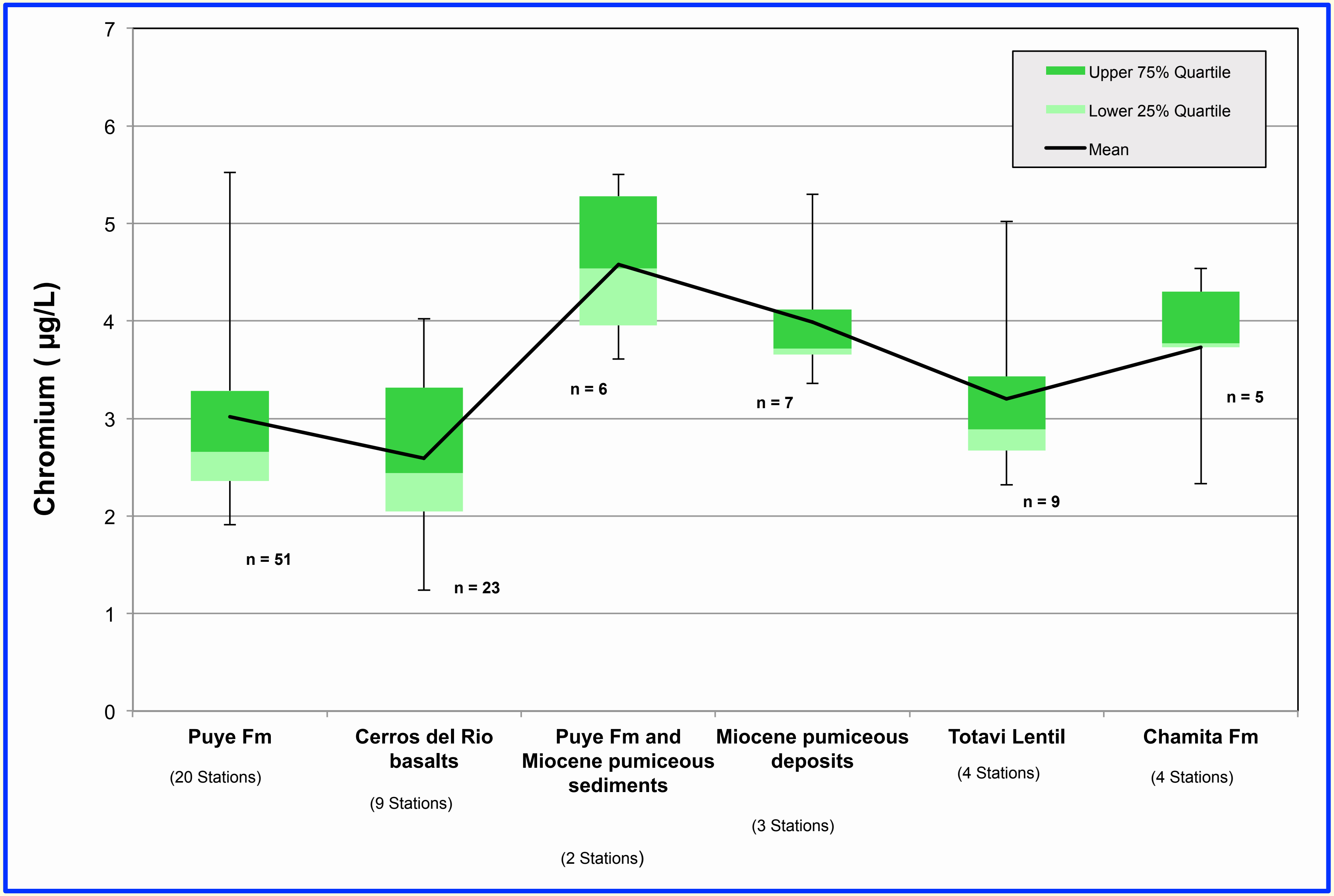
II. Distribution and Transport of Chromium

III. Summary and Conclusions



Mean dissolved chromium concentrations
Contour interval = 0.5 ug/L

Generalized groundwater flow direction in the regional aquifer

Chromium (µg/L)
0
1
2
3
4
5
6
7
Upper 75% Quartile
Lower 25% Quartile
Mean
n = 51
n = 23
n = 6
n = 7
n = 9
n = 5
Puye Fm
(20 Stations)
Cerros del Rio basalts
(9 Stations)
Puye Fm and Miocene pumiceous sediments
(2 Stations)
Miocene pumiceous deposits
(3 Stations)
Totavi Lentil
(4 Stations)
Chamita Fm
(4 Stations)

Photograph of the Jemez Mountains and Pajarito Plateau

(view to the west with industrial sources of chromium(VI) discharges)

Chromium Releases at Technical Area-03, Los Alamos National Laboratory

- Over 15 years of Cr(VI) releases from the TA-03 cooling tower
- Between 31,000 and 72,000 kg of Cr(VI), with a mean of 54,000 kg, were released between 1956 and 1972 into Sandia Canyon
- Most of the Cr(VI) released is from dissociation of potassium dichromate ($K_2Cr_2O_7$)
- Approximately 1100 kg of Cr(VI) reached the regional aquifer (LANL, 2009). This is based on estimates made prior to drilling of R-50 and R-62

Redox Reactions Involving Chromium, Iron, and Manganese

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

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

Coupled Reactions

$$Cr(OH)_3(am) + 3MnO_2(s) + 3Fe^{2+} + 4H_2O = 2H^+ + 3Mn^{2+} + CrO_4^{2-} + 3Fe(OH)_3(am)$$

3 : 1 mole ratio of Fe(II) to Cr(VI) is required to maintain Cr(III) stability

1 : 1 mole ratio of Fe(II) to Mn(IV) is required to maintain Cr(III) stability

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.

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

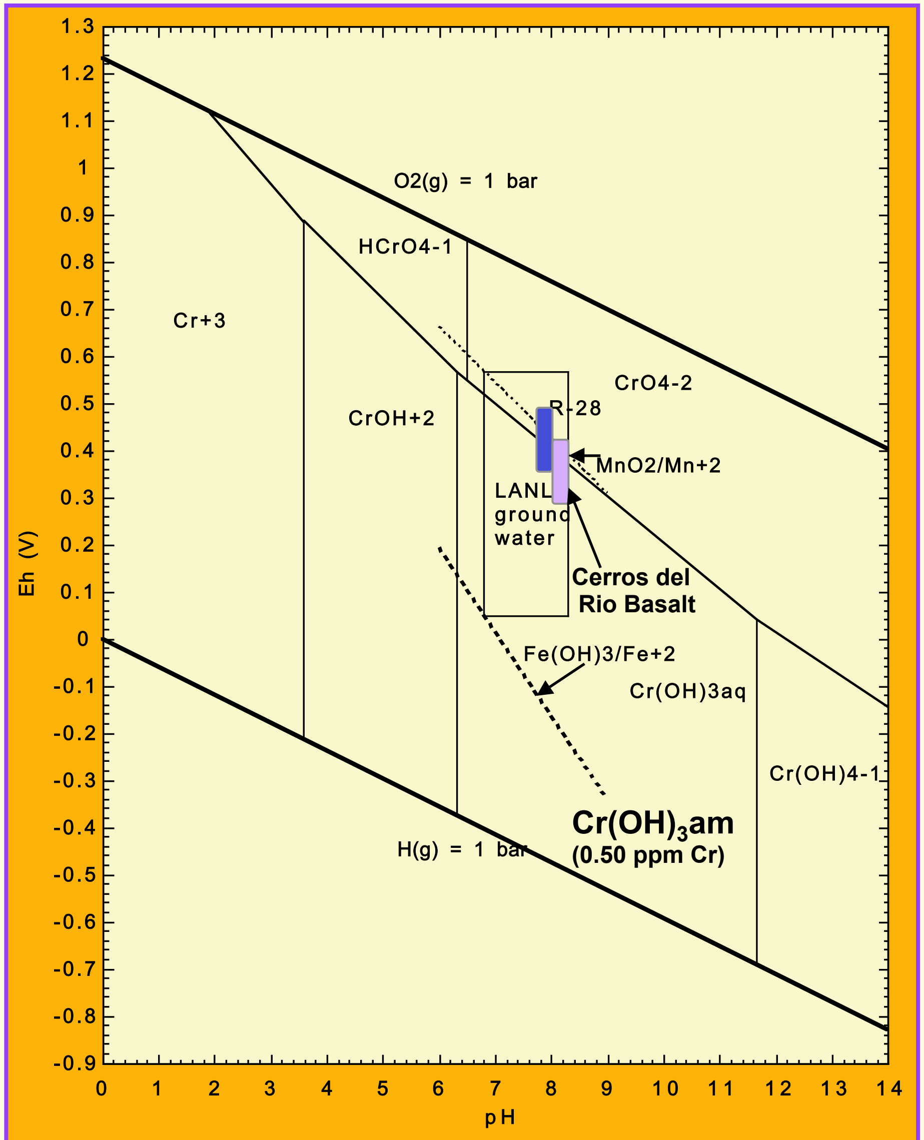
$$Cr(OH)_3(am) + 3MnO_2(s) + H_2O = CrO_4^{2-} + 3MnOOH(s) + 2H^+$$

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, respectiv

Redox Behavior of Chromium in Aqueous Environments

Hydroquinone Dissociation

$C_6H_6O_2 = C_6H_5O_2^- + H^+$

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

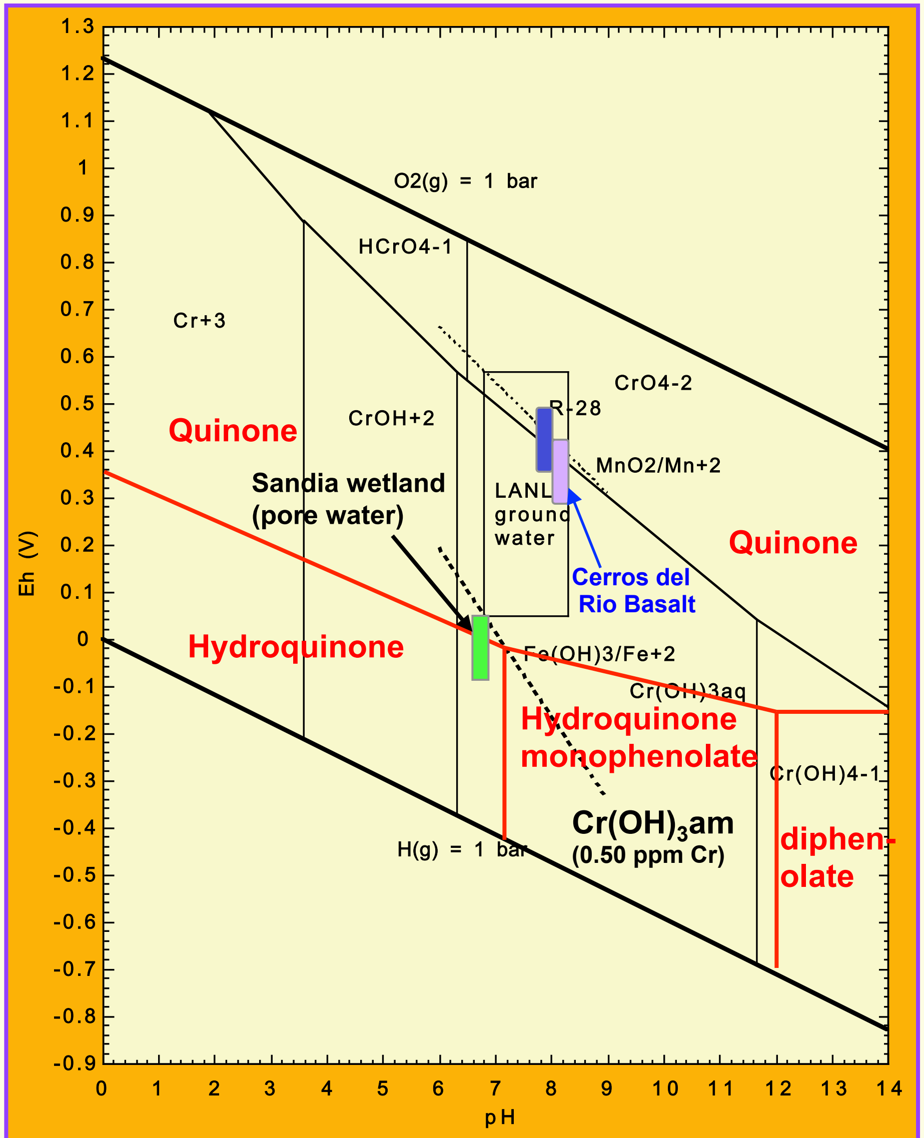
Hydroquinone Oxidation

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

Cr Reduction:

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

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



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, respectiv

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.

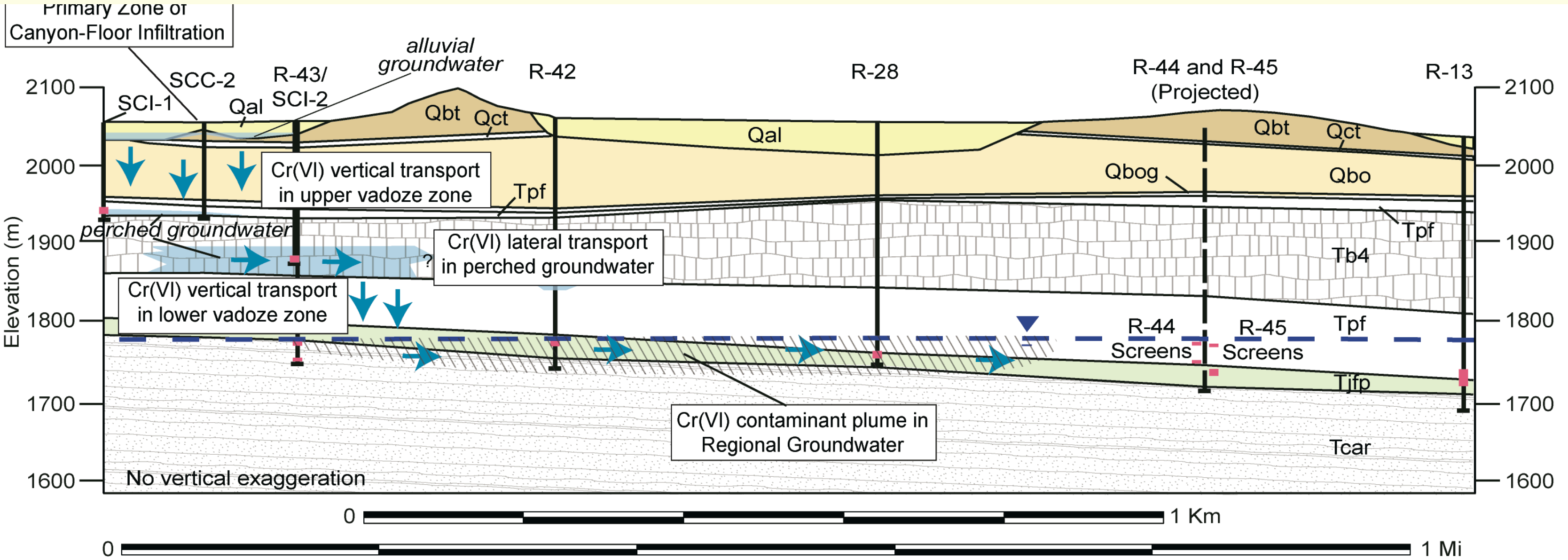
Sandia Canyon Wetland, New Mexico

Sandia Canyon wetland contains >97.3 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 in the wetland. The highest concentration of Cr(III) is 3739 mg/kg associated with dried cattails.

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
$\frac{\text{moles Fe(II)/g soil}}{\text{moles Cr(VI)/g soil}}$ [≥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
$\frac{\text{moles Fe(II)/g soil}}{\text{moles Mn(IV)/g soil}}$ [≥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

A Conceptual Model of Chromium(VI) Transport Through the Vadose Zone and to the Regional Aquifer, Pajarito Plateau, New Mexico



Legend

Quaternary	Qal	Alluvium
	Qbt	Tshirege Member, Bandelier Tuff
	Qct	Cerro Toledo Formation (sedimentary deposits)
	Qbo	Otowi Member, Bandelier Tuff
	Qbog	Guaje Pumice Bed
Pliocene	Tb4	Cerros del Rio basalt
	Tpf	Puye Formation (fanglomerate)
Miocene	Tjfp	Unassigned pumice-rich sedimentary deposits
	Tcar	Chamita Formation (riverine deposits)

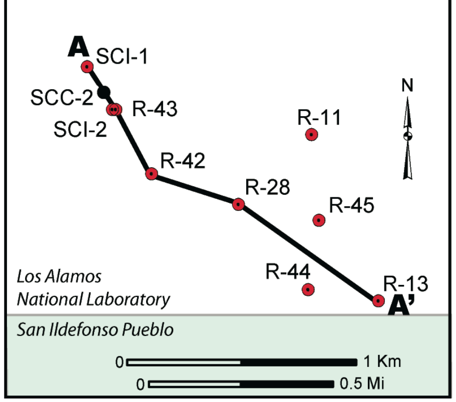
▼ Regional groundwater table

Perched groundwater zone

Groundwater monitoring well (well screen shown in red); dashed where projected

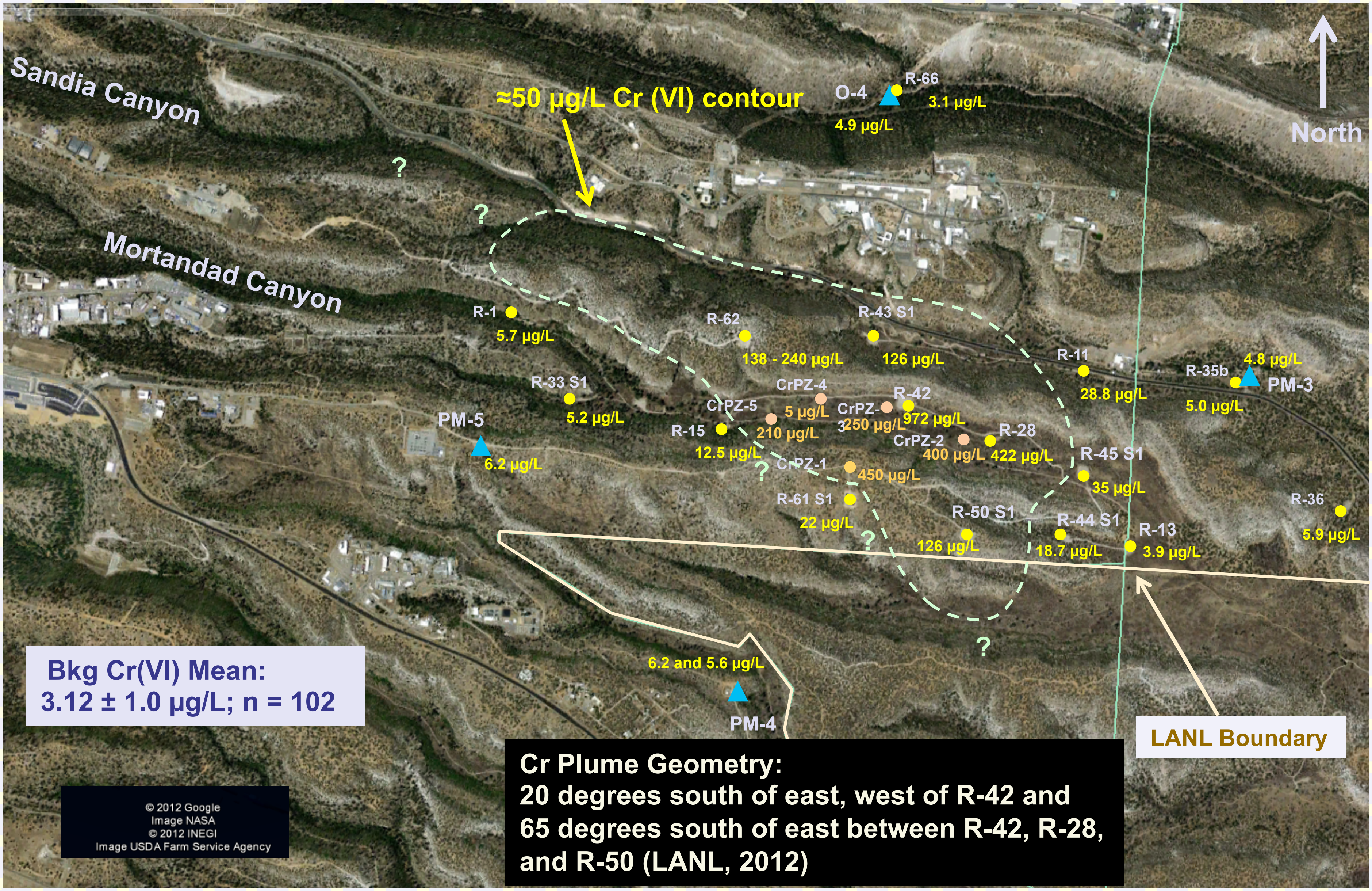
↓ Cr(VI) contaminant pathways

Map View Showing Monitoring Wells and Location of Cross Section



Source: LANL 2012

Concentrations of Cr in the Regional Aquifer, LANL, NM



Bkg Cr(VI) Mean:
3.12 ± 1.0 µg/L; n = 102

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Image NASA
© 2012 INEGI
Image USDA Farm Service Agency

Cr Plume Geometry:
20 degrees south of east, west of R-42 and 65 degrees south of east between R-42, R-28, and R-50 (LANL, 2012)

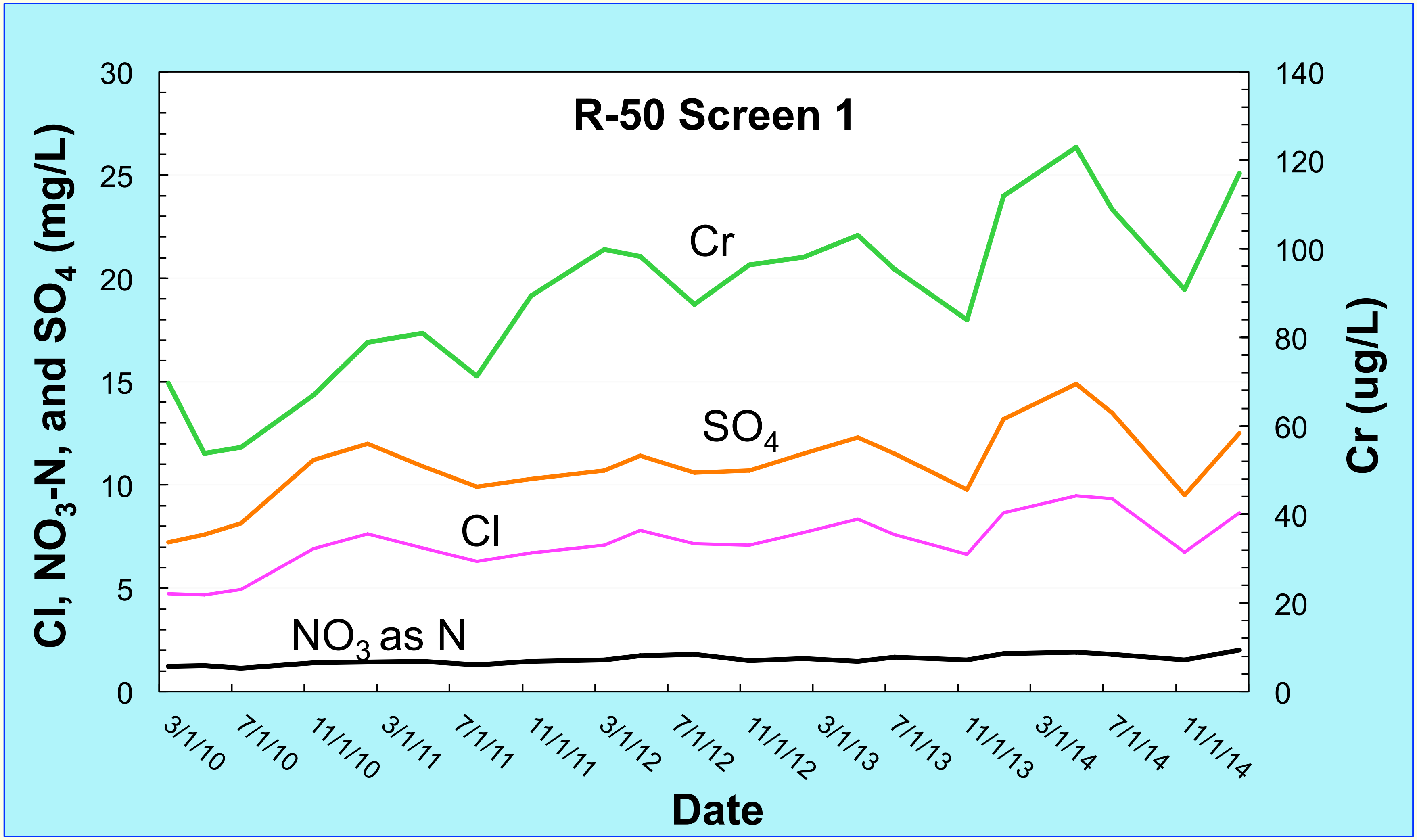
LANL Boundary

▲ **Drinking-Water Production Well**

● **Groundwater Monitoring Well**

0.5 Mile

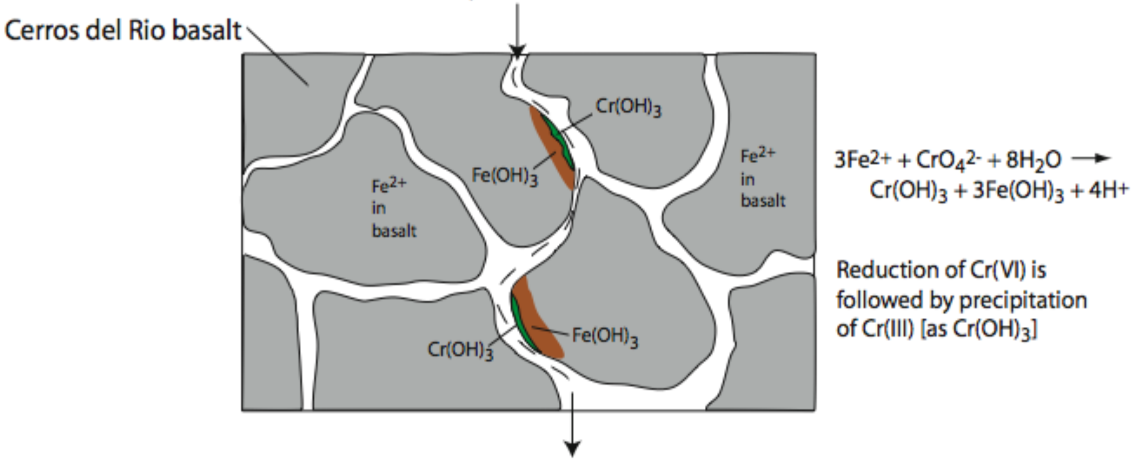
Dissolved Concentrations of Chloride, Chromium, Nitrate-N, and Sulfate at Monitoring Well R-50(1)



Geochemical Conceptual Model for Chromium in the Cerros del Rio Basalt

Chromium Geochemistry within Cerros del Rio Basalt

Input Cr(VI) at higher concentrations
δ^{53}Cr <1 $^{o}/_{oo}$ [very little reduction of Cr(VI)]



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

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

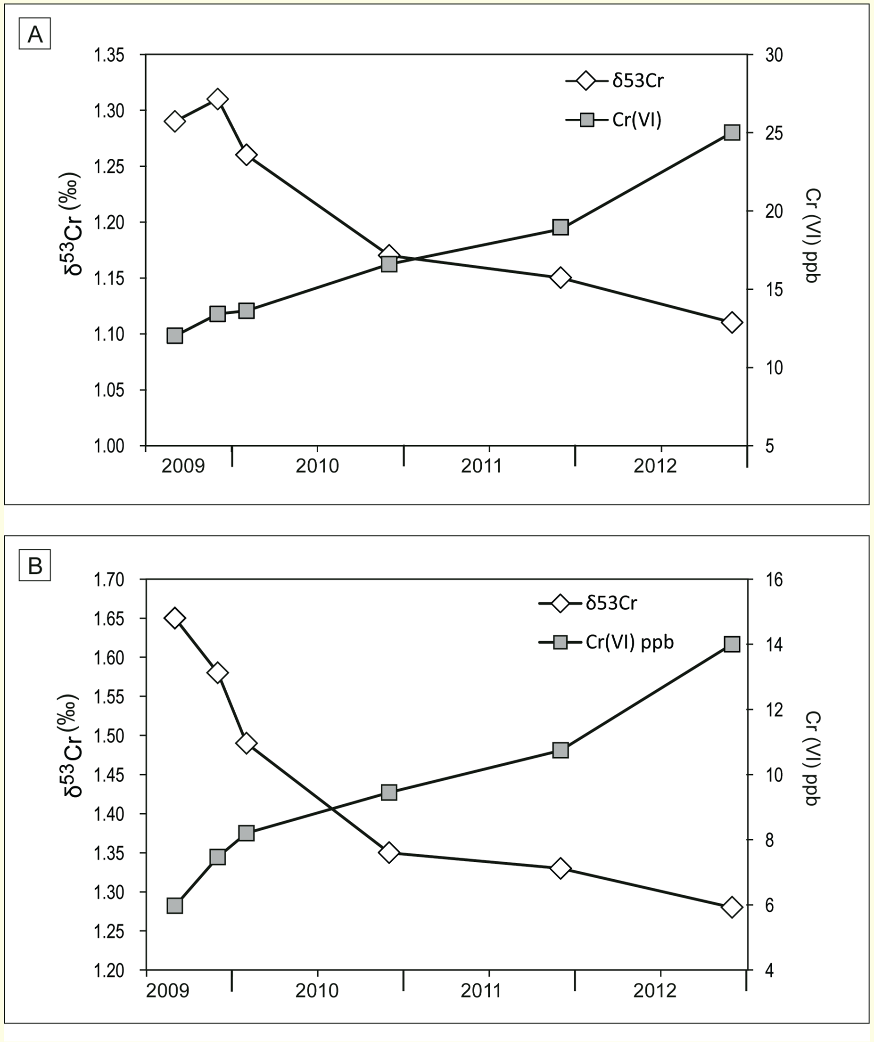
Output Cr(VI) at lower concentrations
δ^{53}Cr up to 3 $^{o}/_{oo}$ [significant reduction of Cr(VI)]

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)

$$^{53}_{52}CrO_4^{2-} + 5H^+ + 3e^- \rightarrow {}_{53}^{52}Cr(OH)_3 + H_2O$$

Concentrations of Chromium(VI) Versus δ^{53}Cr Ratios at Regional Aquifer Well R-45 Screens 1(A) and 2(B), Los Alamos, New Mexico



Source: LANL 2012, J. Heikoop

Evaluation of MNA for Chromium in the Regional Aquifer, Los Alamos National Laboratory, NM

- **Increasing concentrations of Cr(VI) measured during numerous sampling events at various monitoring wells strongly suggest that natural attenuation of this redox-sensitive metal is not taking place to a significant extent.**

- **It is unlikely that natural attenuation would ever result in Cr(VI) concentrations less than 50 μg/L at R-28, R-42, and R-50. Natural attenuation of Cr(VI) in the regional aquifer (Puye Formation and Miocene pumiceous sediments) is strongly suppressed by: *(next slide)***

Evaluation of MNA for Chromium in the Regional Aquifer, Los Alamos National Laboratory, NM

- **Insufficient concentrations of electron donors or reducing agents such as magnetite, metal sulfide phases including pyrite, and solid organic matter;**
- **Stability of strongly oxidizing groundwater conditions in the presence of dissolved oxygen, manganese(IV), and iron(III);**
- **High aqueous solubility of metal-Cr(VI) phases; and**
- **A low adsorption capacity of regional aquifer sediments for Cr(VI) under basic pH conditions.**

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

- **Residual chromium (Cr) occurs in the unsaturated zone beneath Sandia and Mortandad Canyons, New Mexico.**
- **Partial adsorption of residual Cr onto hydrous ferric oxide has been quantified by soil leach experiments and geochemical modeling.**
- **Transport of Cr(VI) occurs under relatively oxidizing and basic pH conditions within the vadose zone and regional aquifer.**
- **Stable isotopes of Cr are a useful tool along with groundwater and aquifer chemistry, groundwater residence times, and knowledge of groundwater-flow paths for quantifying natural attenuation of Cr.**
- **A fraction of anthropogenic Cr(VI) has reached the regional aquifer with dissolved concentrations up to 1240 μg/L.**

Summary and Conclusions

- **Soluble chromium(VI) is stable in the regional-aquifer system characterized by strongly oxidizing conditions with respect to iron, dissolved oxygen, and manganese.**
- **Chromium is migrating at nearly the same rate of groundwater flow within the regional aquifer (Puye Formation and Miocene pumiceous sediments).**
- **The mass, nature, and extent of chromium contamination in the vadose zone and regional aquifer is not completely known.**
- **Natural attenuation of chromium(VI) is not an effective process taking place in the regional-aquifer system.**
- **Successful aquifer remediation of chromium in the regional aquifer requires complete understanding of:**
  - **Nature and extent of contamination and**
  - **Geochemical, biochemical, and hydrologic characteristics.**

Supplemental Material

Analytical Methods

Major Ions

Ion chromatography, titration, and inductively coupled plasma-optical emission spectroscopy

Trace Elements

Inductively coupled plasma-optical emission spectroscopy and (high resolution) inductively coupled plasma-mass spectrometry

Oxyanions

Liquid chromatography/mass spectrometry-mass/spectrometry

Analytical Methods

Stable Isotopes

Isotope ratio mass spectrometry ($\delta^{2}H$, $\delta^{18}O$, $\delta^{15}N$, and $^{13}\delta C$)

^{129}Iodine and ^{36}Chlorine

Accelerator mass spectrometry

^{239}Plutonium and Tritium

Alpha spectrometry

Electrolytic enrichment and liquid scintillation

Calculated Rates of Chromium Transport in the Regional Aquifer, Pajarito Plateau, New Mexico

Cr migration rate = groundwater-flow rate (feet/year)/R_f.

(73 feet/year)/1.5 = 49 feet/year;

(131 feet/year)/1.5 = 83 feet/year; and

(164 feet/year)/1.5 = 109 feet/year.

The most representative Cr transport rates most likely range from 83 to 109 feet/year in the regional aquifer at R-28. This range is based on extensive monitoring data provided by LANL (2012) and NMED and Cr trend analysis.

R_f is the retardation factor (1 + pKd/n_e) where p(1.5g/cm^3), Kd(0.1 mL/g), and n_e(0.30) are bulk density, distribution coefficient, and effective porosity, respectively. R_f = 1.5 for the above calculations.

Concentrations of Chromium(VI) Versus δ^{53}Cr Ratios in Groundwater, Los Alamos, New Mexico

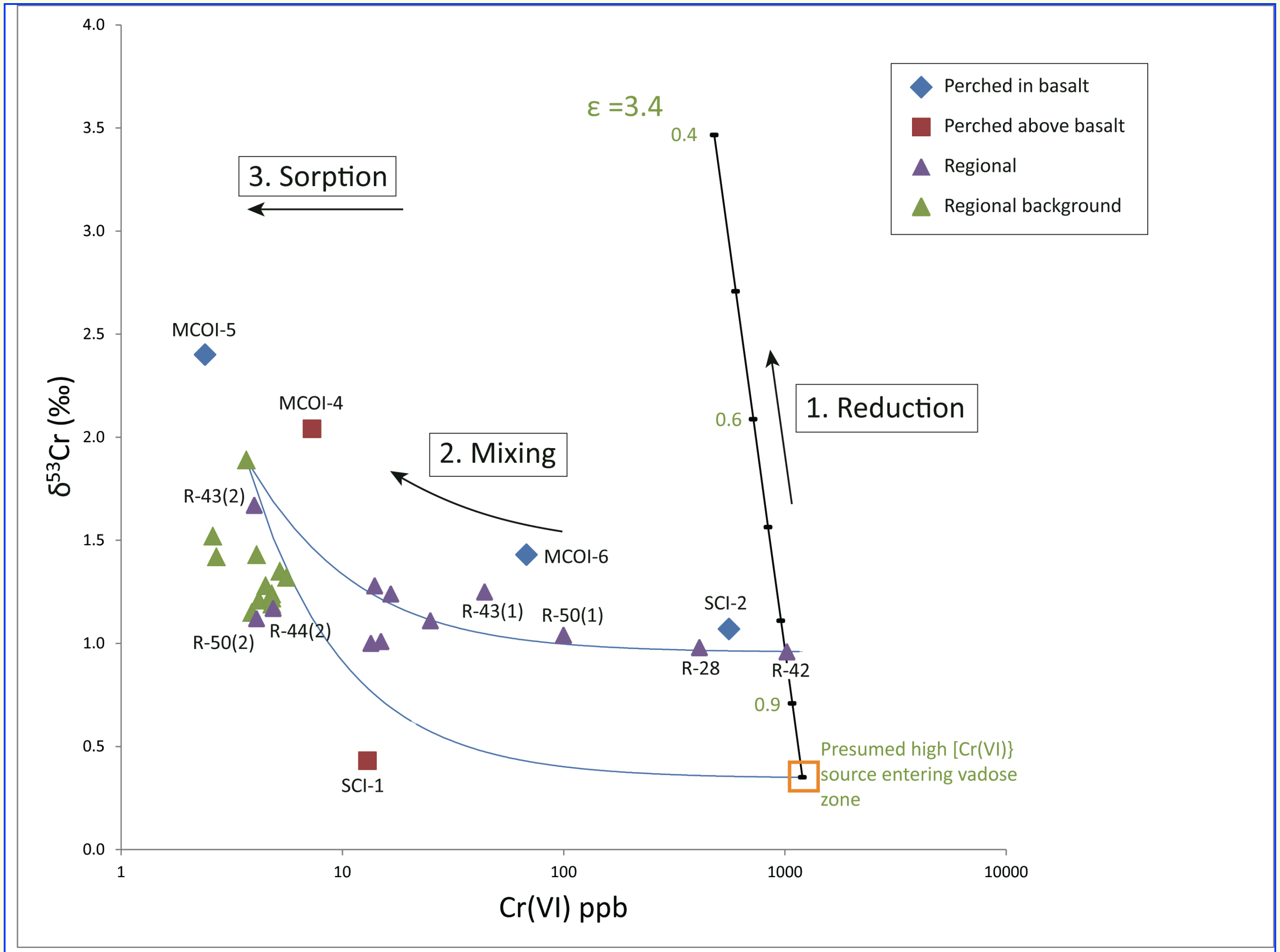
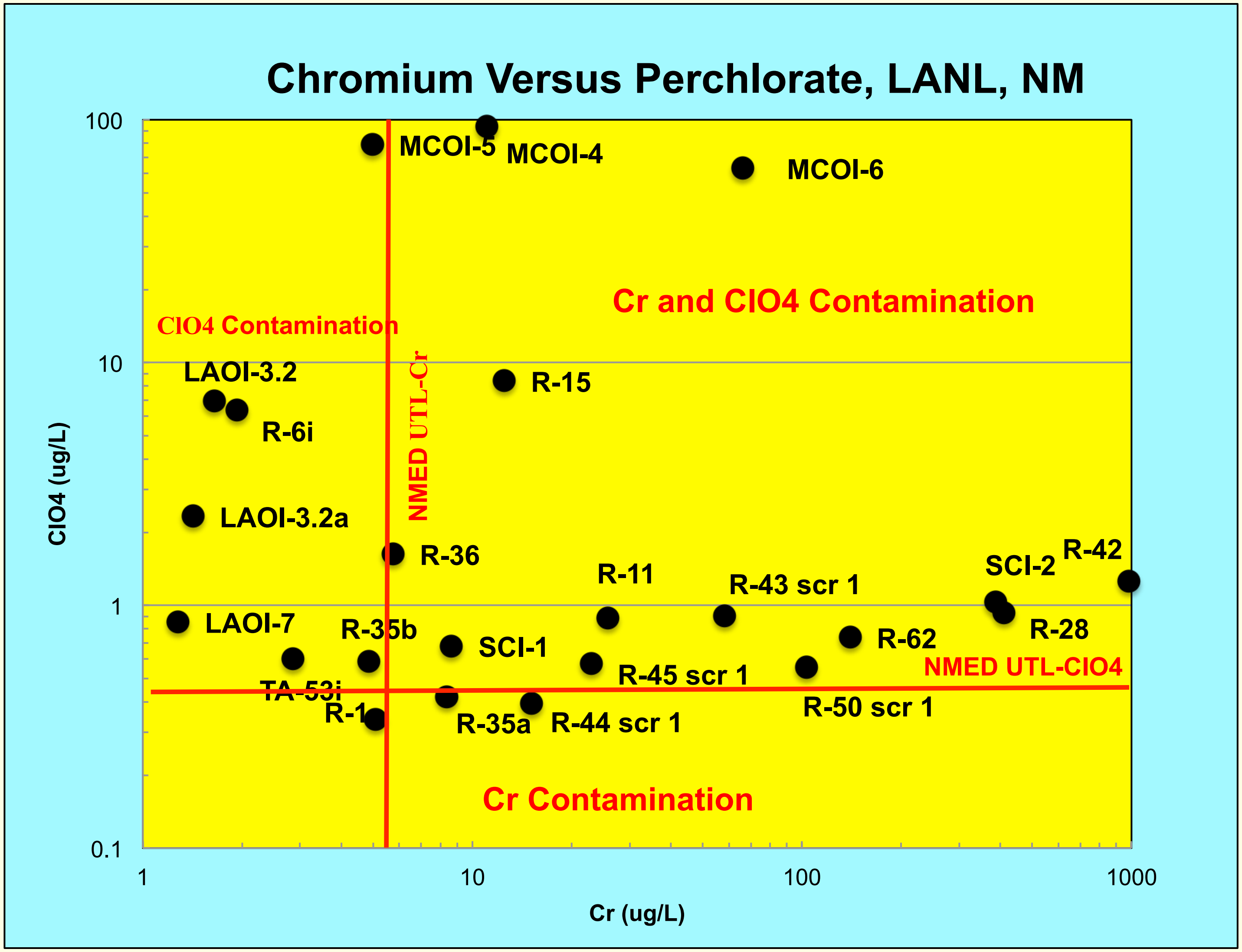


Figure 3

Source: LANL, 2012 (J. Heikoop)

CHROMIUM VERSUS PERCHLORATE, LANL



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