AQUEOUS GEOCHEMISTRY, TRANSPORT, AND REMEDIATION OF CHROMIUM IN AN OXIDIZING AQUIFER SYSTEM, LOS ALAMOS, NEW MEXICO

BY

Patrick Longmire, Megan Green, David Fellenz,
Kim Granzow, and Stephen Yanicak

DOE OVERSIGHT BUREAU
NEW MEXICO ENVIRONMENT DEPARTMENT

1183 Diamond Drive, Suite B
Los Alamos, New Mexico 87544

Aqueous Geochemistry, Transport, and Remediation of Chromium at Los Alamos National Laboratory

We thank:

TerranearPMC for sampling numerous monitoring wells for several decades at LANL.

The Chromium Technical Team consisting of NMED, DOE, and LANL staff.

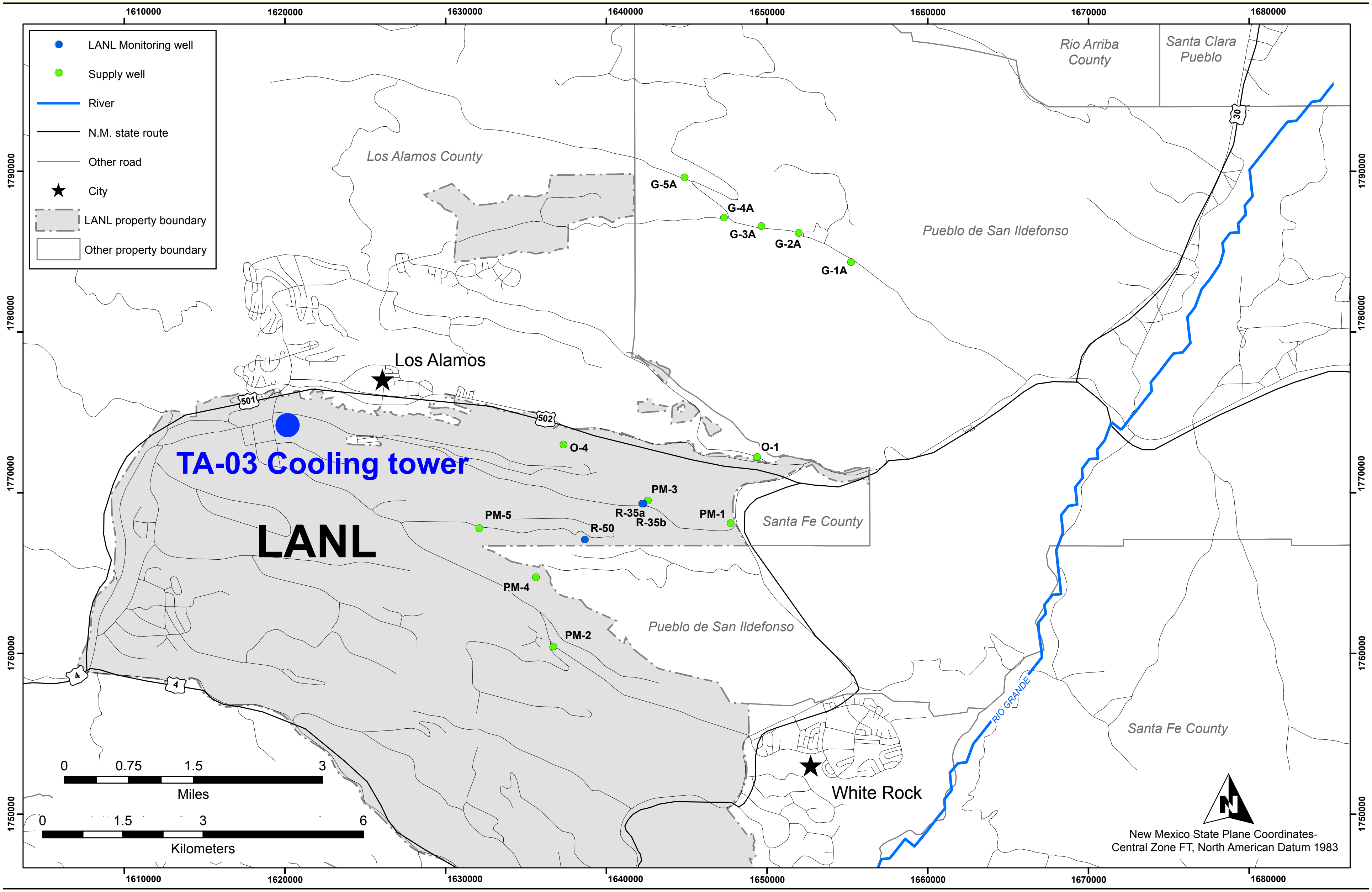
Pueblo de San Ildefonso for granting access to monitoring well SIMR-2.

Acknowledgment: "This material is based upon work supported by the Department of Energy Office of Environmental Management under Award Number *DE-EM0002420*."

Aqueous Geochemistry, Transport, and Remediation of Chromium at Los Alamos National Laboratory

- **Introduction**
- **Sources of potassium dichromate**
- **Distribution of chromium in the regional aquifer**
- **Natural attenuation**
- ***In situ* remediation**
- **Summary and conclusions**

Location Map of Los Alamos County Supply Wells



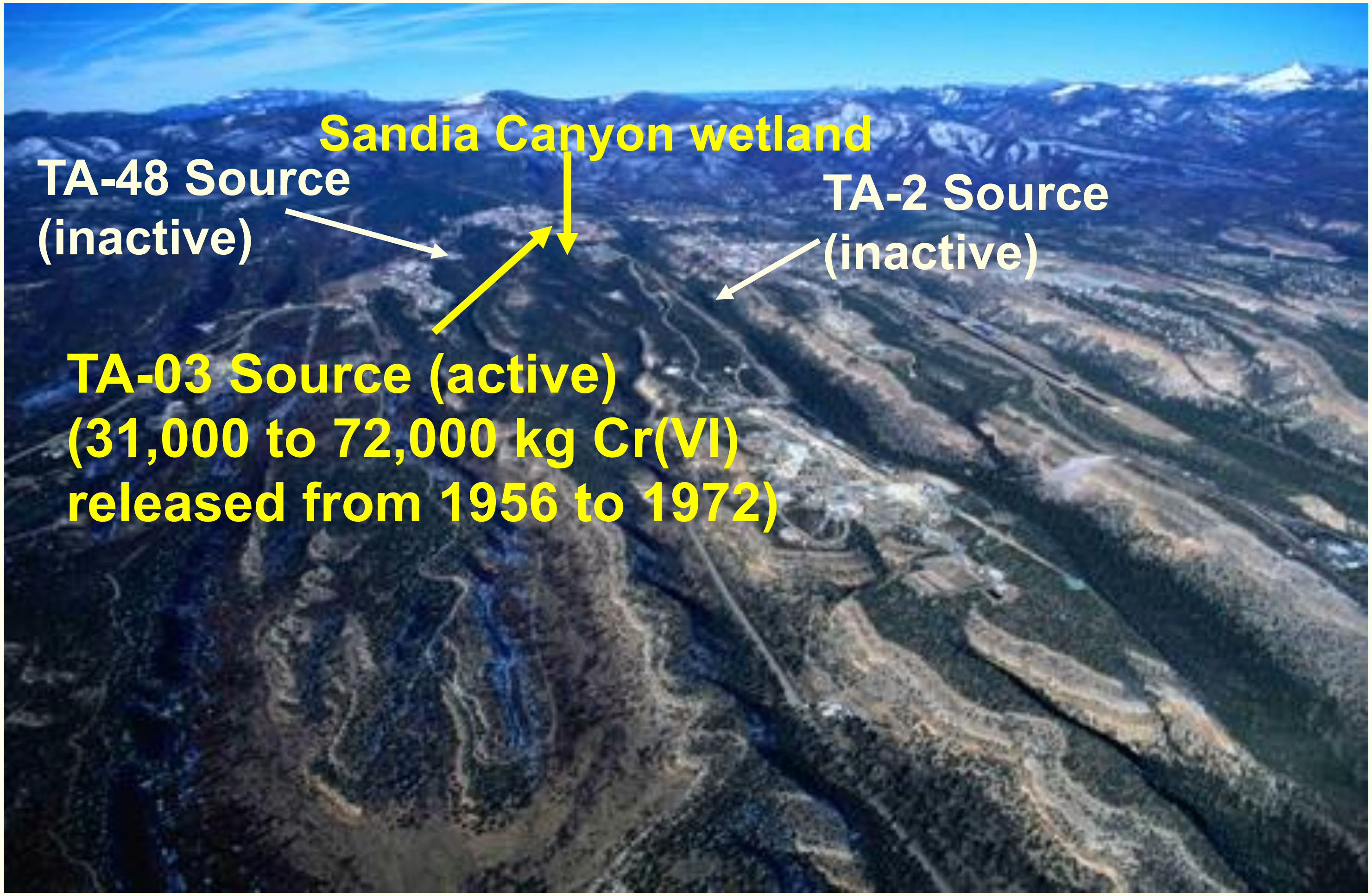
Chromium Releases at Technical Area-03, Los Alamos National Laboratory

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

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

Chromate is from dissociation of potassium dichromate ($K_2Cr_2O_7$).

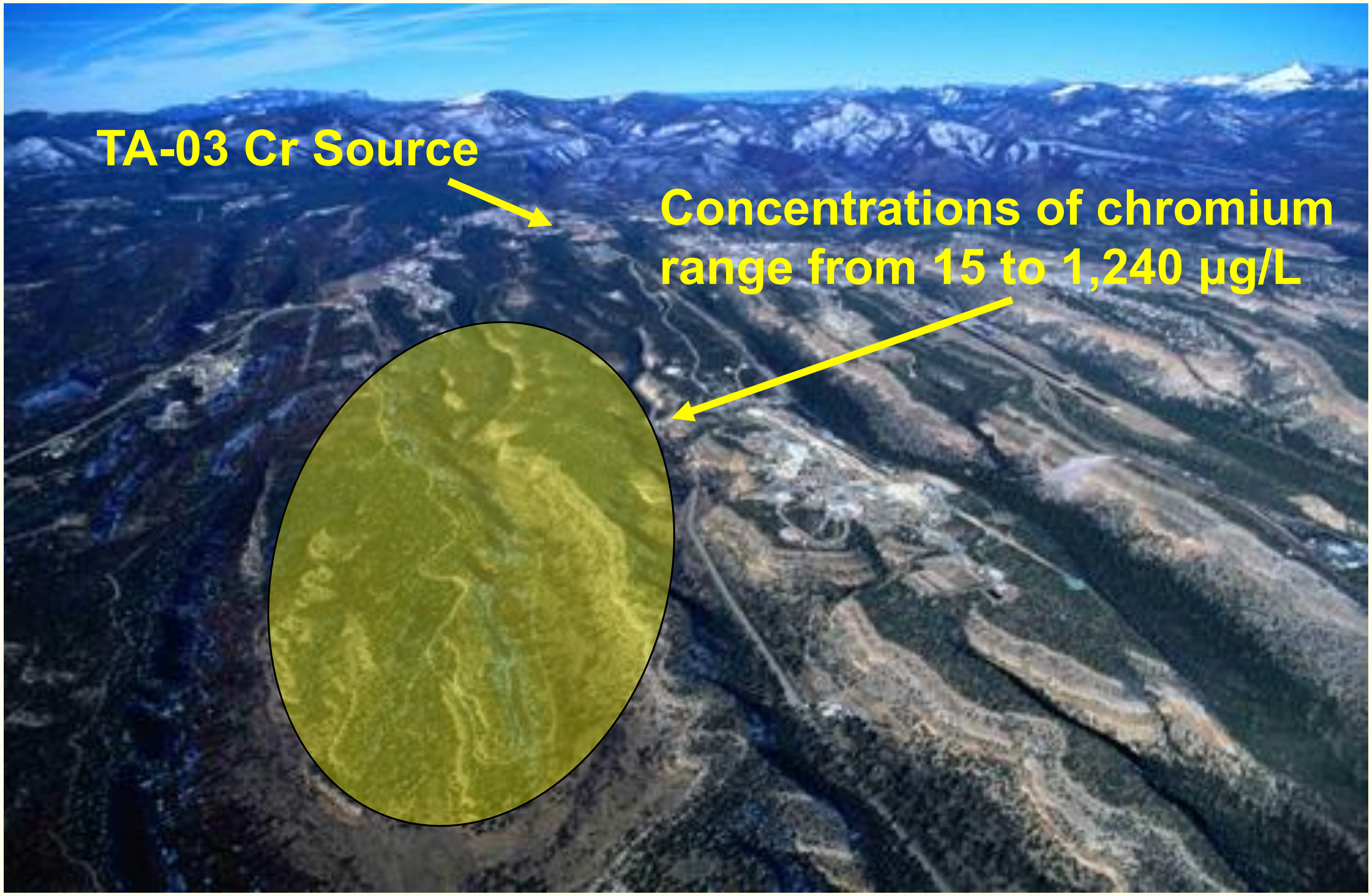
Photograph of the Jemez Mountains and Pajarito Plateau
(view to the west with industrial sources of chromium(VI) discharges)



Sandia Canyon, New Mexico

Sandia Canyon wetland contains 97.3 to 99.9 percent Cr(III) of 11,000 kg Cr (median) with a range of 5700 to 27,000 kg Cr.

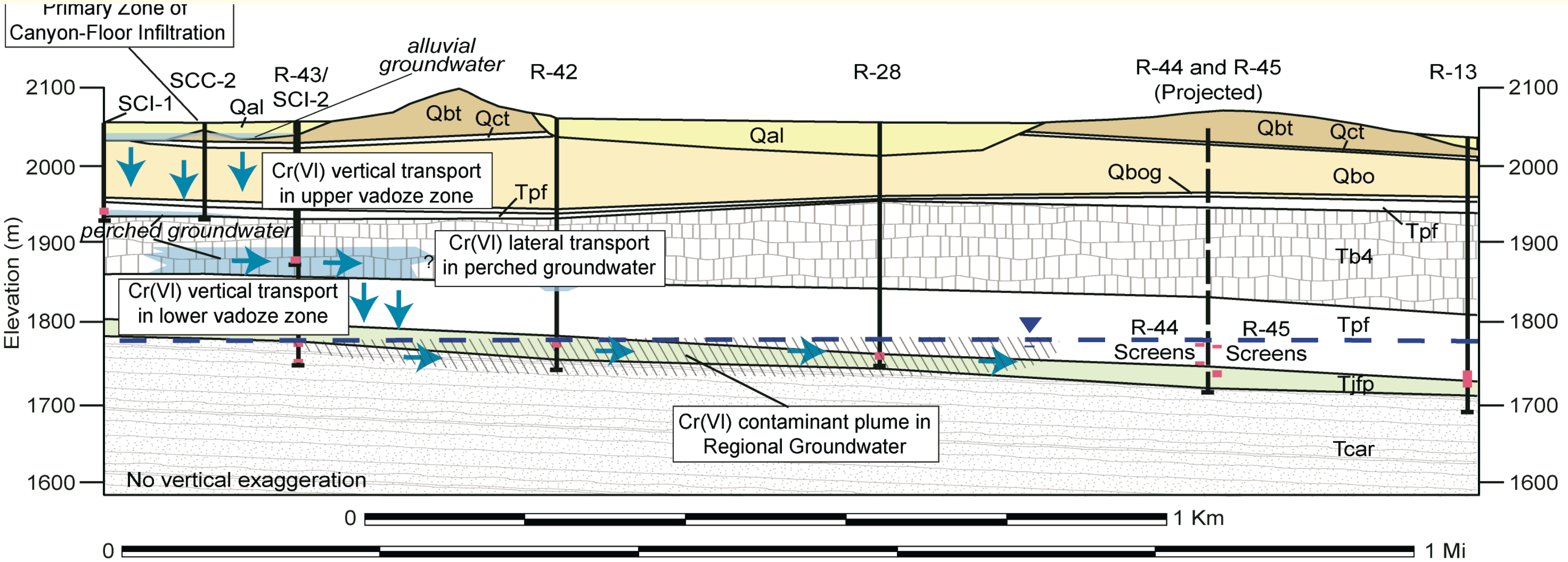
Chromium Plume Boundary in the Regional Aquifer



TA-03 Cr Source

Concentrations of chromium range from 15 to 1,240 µg/L

Conceptual Model of Chromium(VI) Transport Through the Vadose Zone and to the Regional Aquifer, Los Alamos, New Mexico



Cr(VI) vertical transport in upper vadoze zone

Cr(VI) lateral transport in perched groundwater

Cr(VI) vertical transport in lower vadoze zone

Cr(VI) contaminant plume in Regional Groundwater

No vertical exaggeration

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)

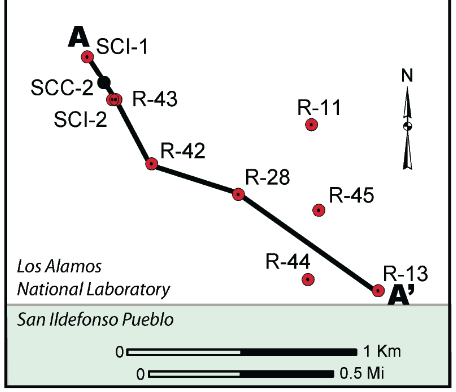
▼ Regional groundwater table

▨ Perched groundwater zone

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

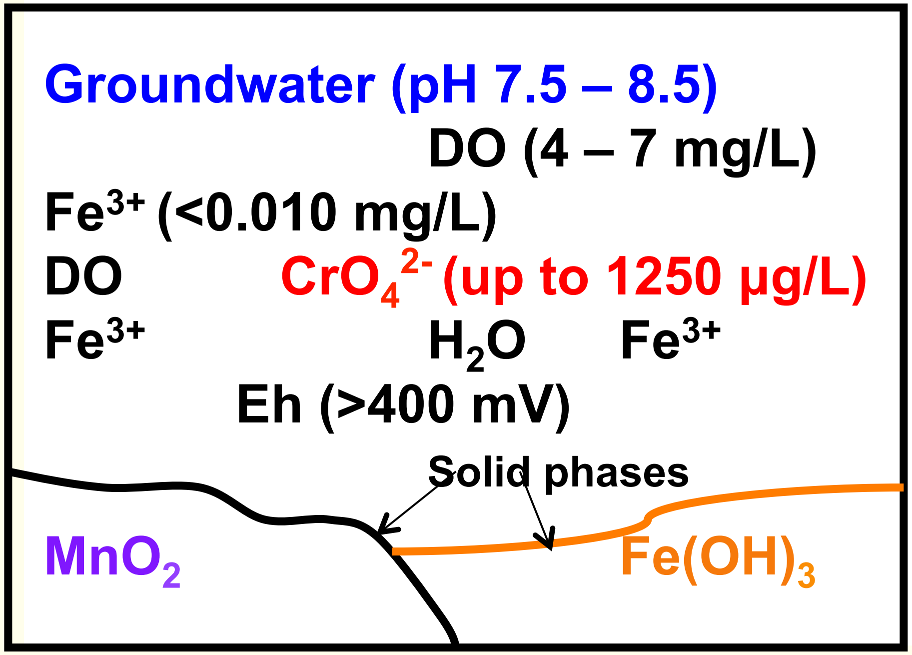
↓ Cr(VI) contaminant pathways

Map View Showing Monitoring Wells and Location of Cross Section



Source: LANL 2012

Chromium(VI) Stability in Aquifer Systems Containing Oxidized Minerals and Oxidizing Groundwater



Groundwater (pH 7.5 – 8.5)

DO (4 – 7 mg/L)

Fe^{3+} (<0.010 mg/L)

DO CrO_4^{2-} (up to 1250 µg/L)

Fe^{3+} H_2O Fe^{3+}

Eh (>400 mV)

Solid phases

MnO_2 $Fe(OH)_3$

Aquifer System Characteristics

Oxidized iron [Fe^{3+}]
Oxidized iron [$Fe(OH)_3$]
Oxidized manganese [MnO_2]

Oxidized chromium [CrO_4^{2-}] (chromate)

Dissolved oxygen (DO)

Analytical Methods Used by NMED

Total Dissolved Chromium and Other Trace Elements

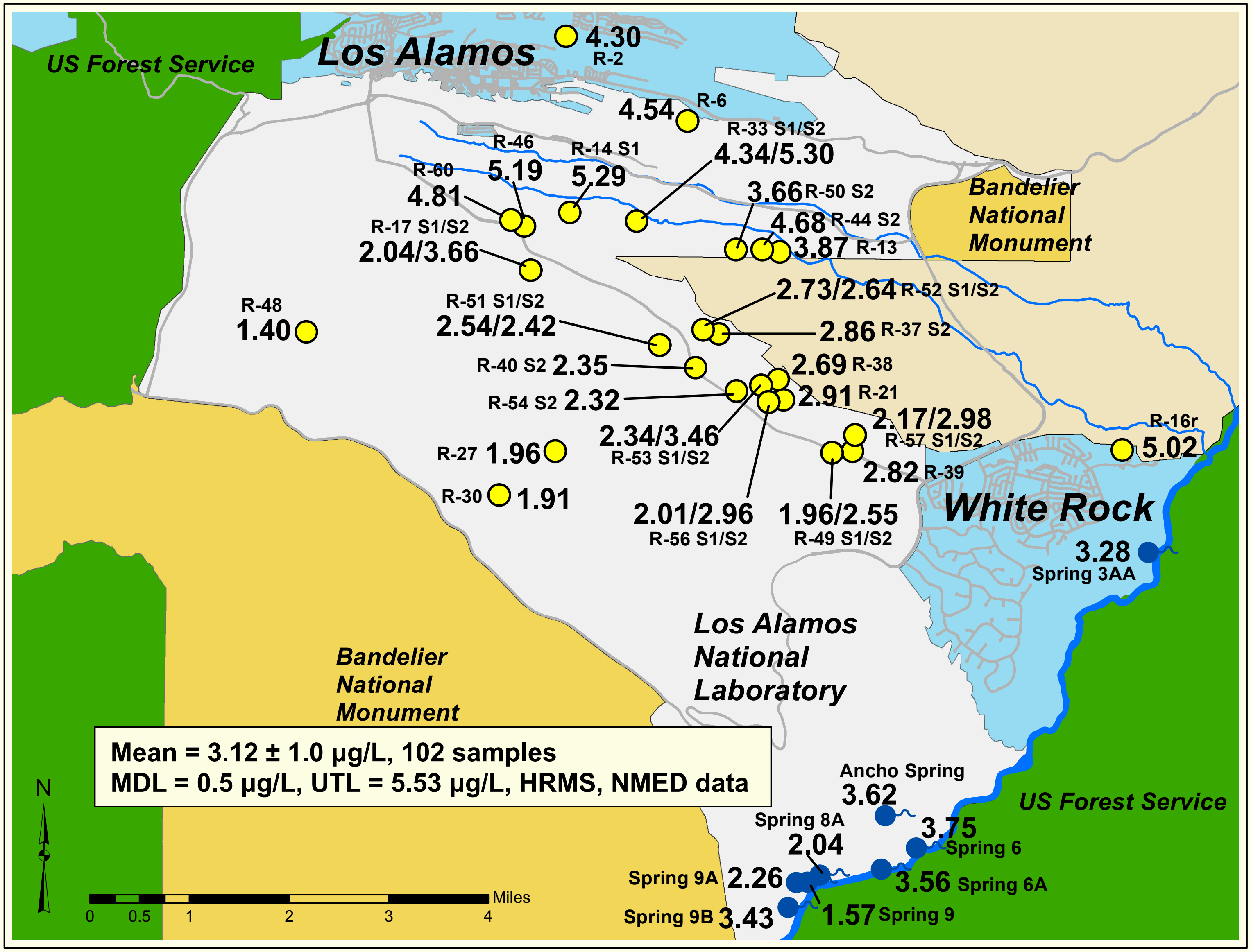
High-resolution inductively coupled plasma-mass spectrometry

Inductively coupled plasma-optical emission spectroscopy

Major-trace Ions

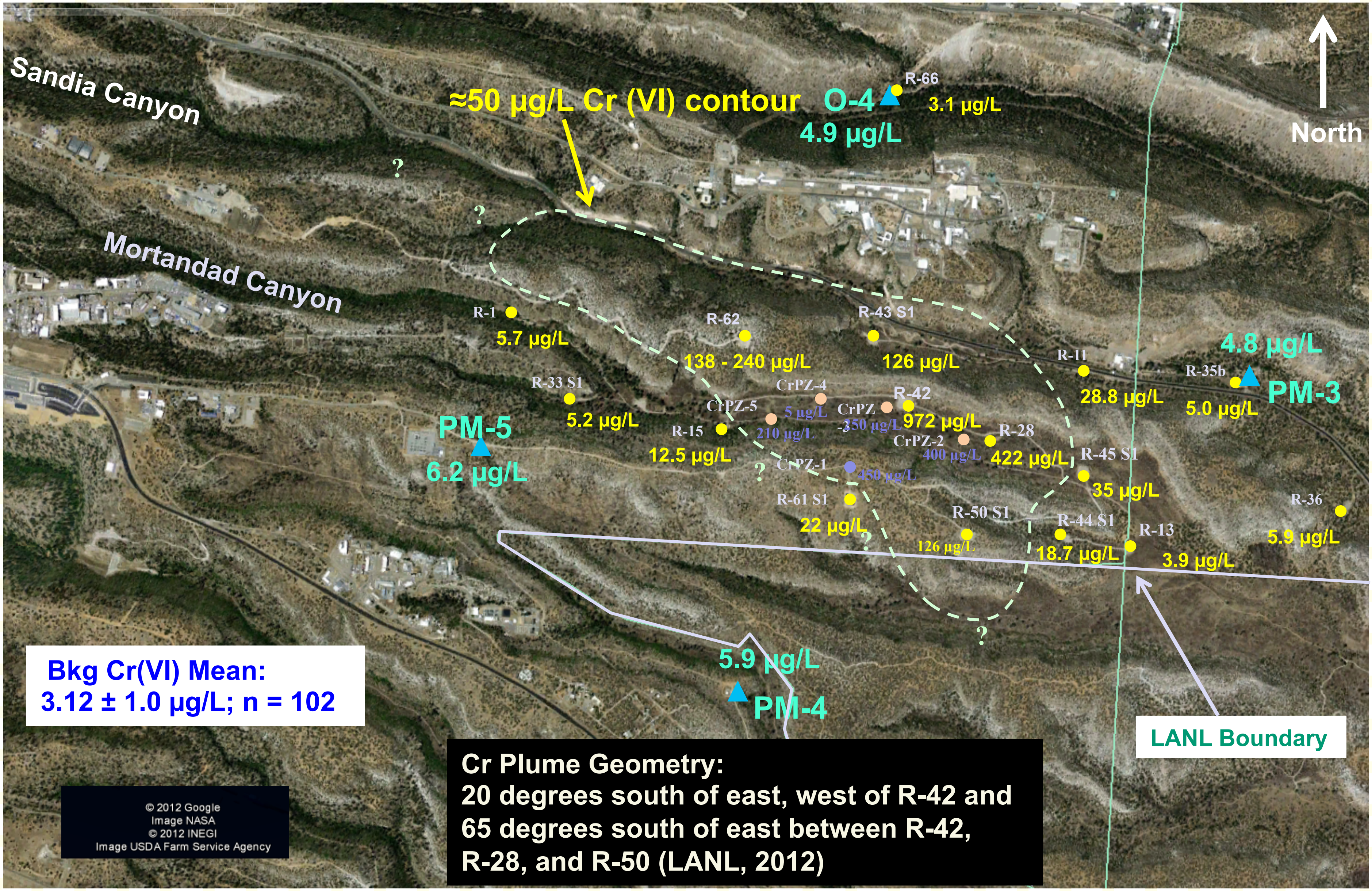
Ion chromatography, titration, and inductively coupled plasma-optical emission spectroscopy

Background Concentrations of Dissolved Chromium (µg/L) in the Regional Aquifer, Los Alamos National Laboratory



Mean = 3.12 ± 1.0 µg/L, 102 samples
MDL = 0.5 µg/L, UTL = 5.53 µg/L, HRMS, NMED data

Dissolved Concentrations of Cr in the Regional Aquifer, LANL, NM



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

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)

▲ **Drinking-Water Production Well**

● **Groundwater Monitoring Well**

0.5 Mile

Calculated Rates of Chromium Transport in the Regional Aquifer, Los Alamos, New Mexico

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

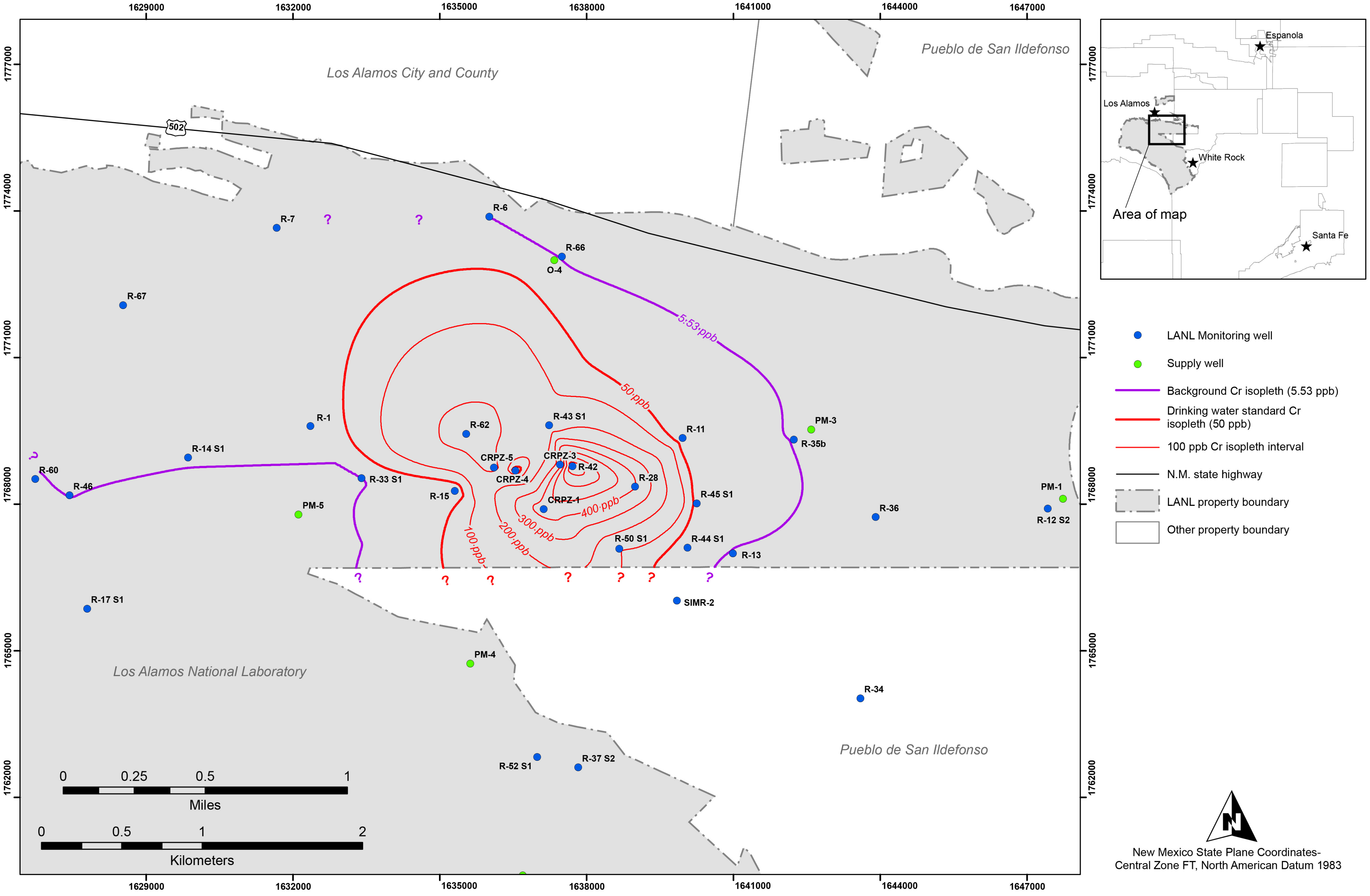
(131 feet/year)/1.1 = 119 feet/year and

(164 feet/year)/1.1 = 149 feet/year.

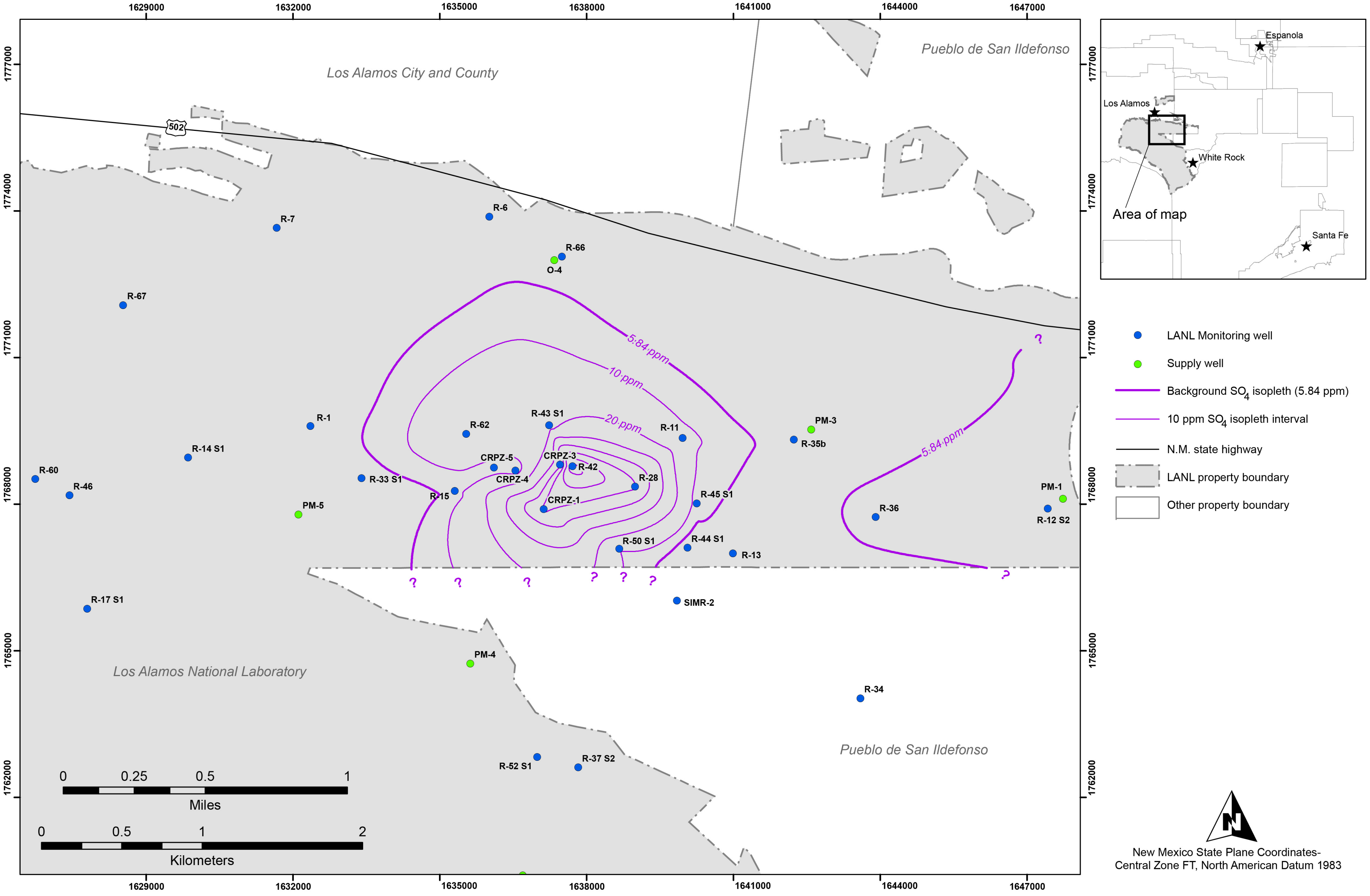
The most representative Cr transport rates most likely range from 119 to 149 feet/year in the regional aquifer at R-28. This range is based on experimental data provided by LANL (2015) and NMED geochemical modeling analysis.

R_f is the retardation factor (1 + pKd/n) where p ($1.5 g/cm^3$), Kd (0.1 mL/g), and n (0.30) are bulk density, distribution coefficient, and effective porosity, respectively. R_f = 1.1 for the above calculations.

Concentrations of Total Dissolved Chromium in the Regional Aquifer, LANL



Concentrations of Sulfate in the Regional Aquifer, LANL



NATURAL ATTENUATION OF HEXAVALENT CHROMIUM

Palmer and Puls (1994) recommend that the following data and information be collected to support chromate reduction:

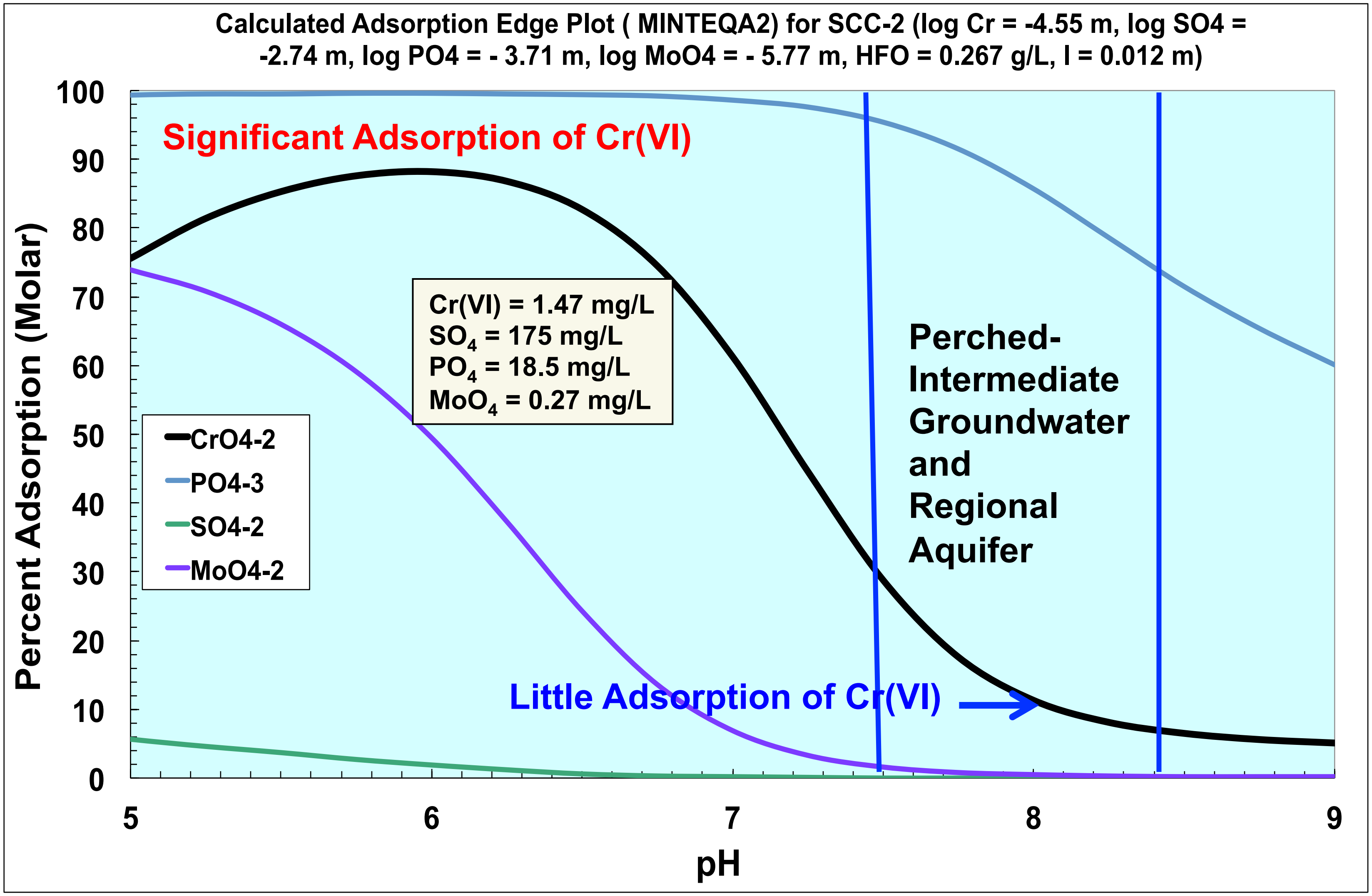
- **There are natural reductants (electron donors) present in the groundwater (Fe(II), organic carbon);**
- **The amount of Cr(VI) and other reactive constituents does not exceed the reductive capacity of the aquifer system;**
- **The time scale required to achieve the reduction of Cr(VI) to the target concentration is less than the time scale to transport dissolved Cr(VI) from the source to the point of compliance;**

NATURAL ATTENUATION OF HEXAVALENT CHROMIUM

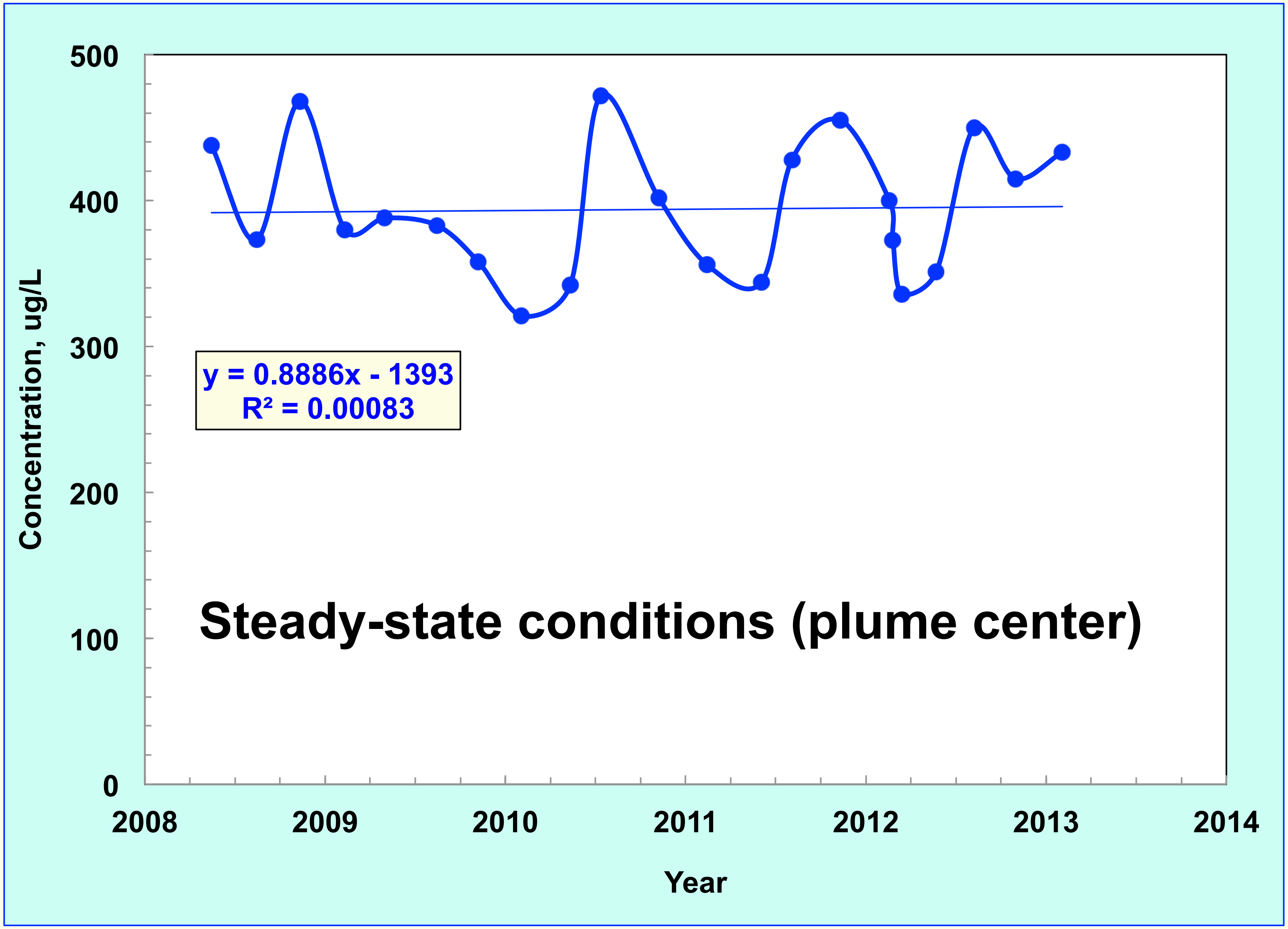
Palmer and Puls (1994) recommend that the following data and information be collected to support chromate reduction:

- **The Cr(III) solid phase will remain immobile; and**
- **There is no net reoxidation of Cr(III) to Cr(VI) by electron acceptors including Mn(IV) solids and dissolved oxygen.**

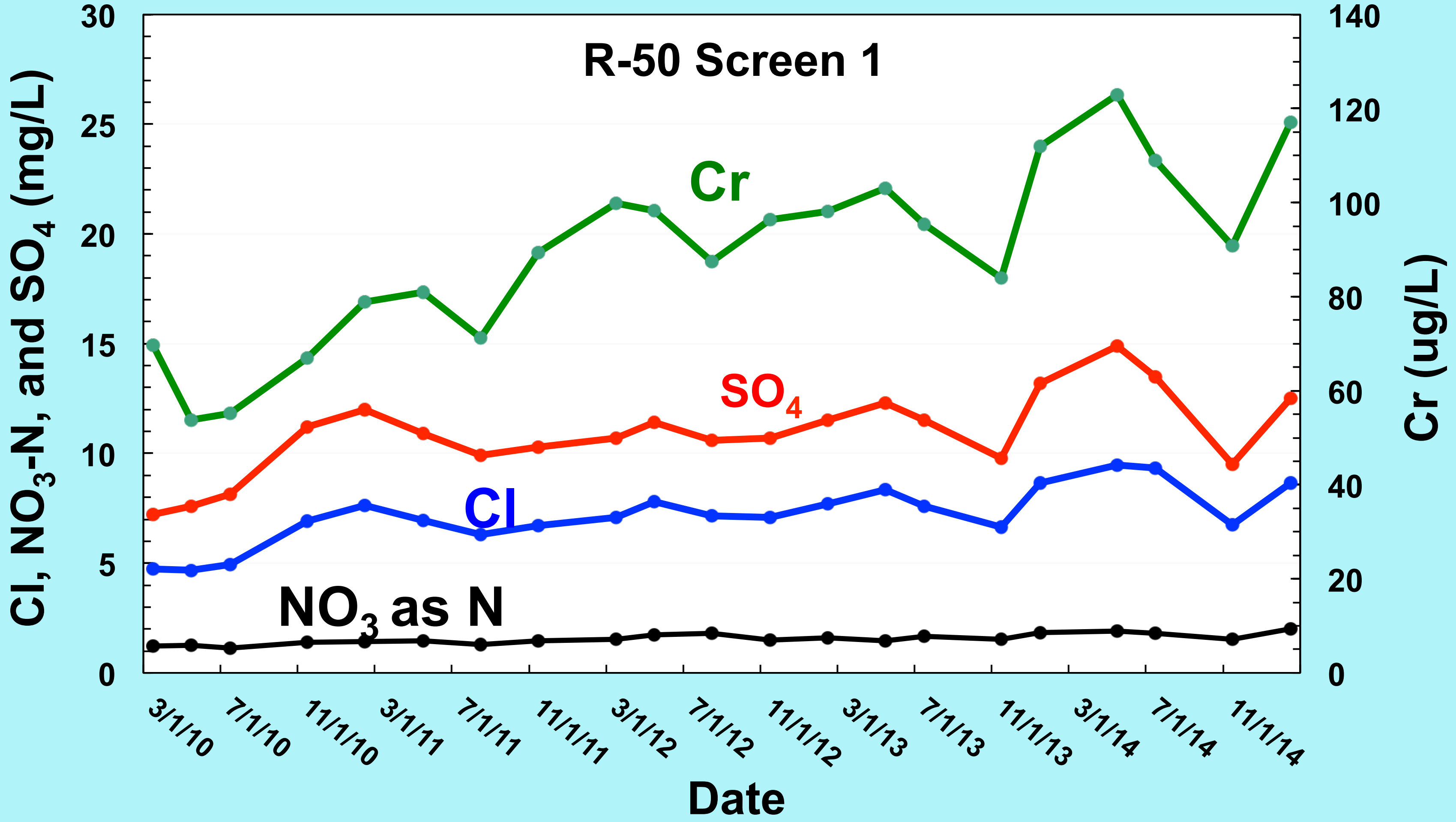
Calculated Adsorption Edge Plot Using MINTEQA2 for the Unsaturated Zone, Sandia Canyon, New Mexico



Dissolved Concentrations of Chromium at Regional Aquifer Well R-28, Los Alamos, New Mexico



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



Evaluation of Monitored Natural Attenuation for Chromium in the Regional Aquifer at LANL

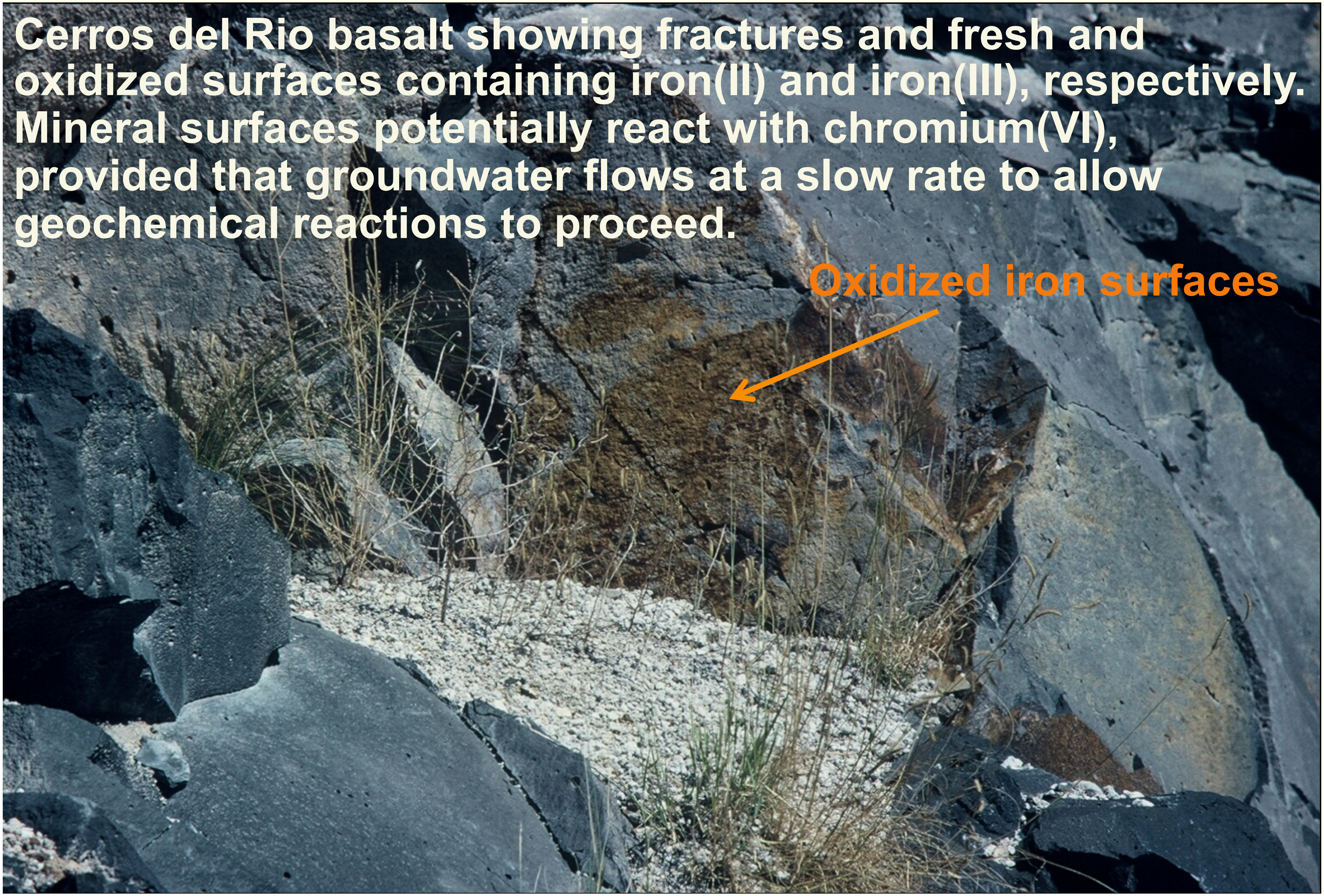
- **Increasing concentrations of Cr(VI) measured during numerous sampling events at various monitoring wells strongly suggest that natural attenuation of this redox-sensitive metal is not taking place to a significant extent.**

- **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 Monitored Natural Attenuation for Chromium in the Regional Aquifer at LANL

- 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.

Outcrop of Cerros del Rio Basalt, Perched Zones



Cerros del Rio basalt showing fractures and fresh and oxidized surfaces containing iron(II) and iron(III), respectively. Mineral surfaces potentially react with chromium(VI), provided that groundwater flows at a slow rate to allow geochemical reactions to proceed.

Fractionation of δ^{53}Cr During Chromate Reduction

$$^{53/52}CrO_4^{2-} + 3Fe^{2+} + 8H_2O \rightarrow$$

$$3Fe(OH)_3(am) + {}^{53/52}Cr(OH)_3(am) + 4H^+$$

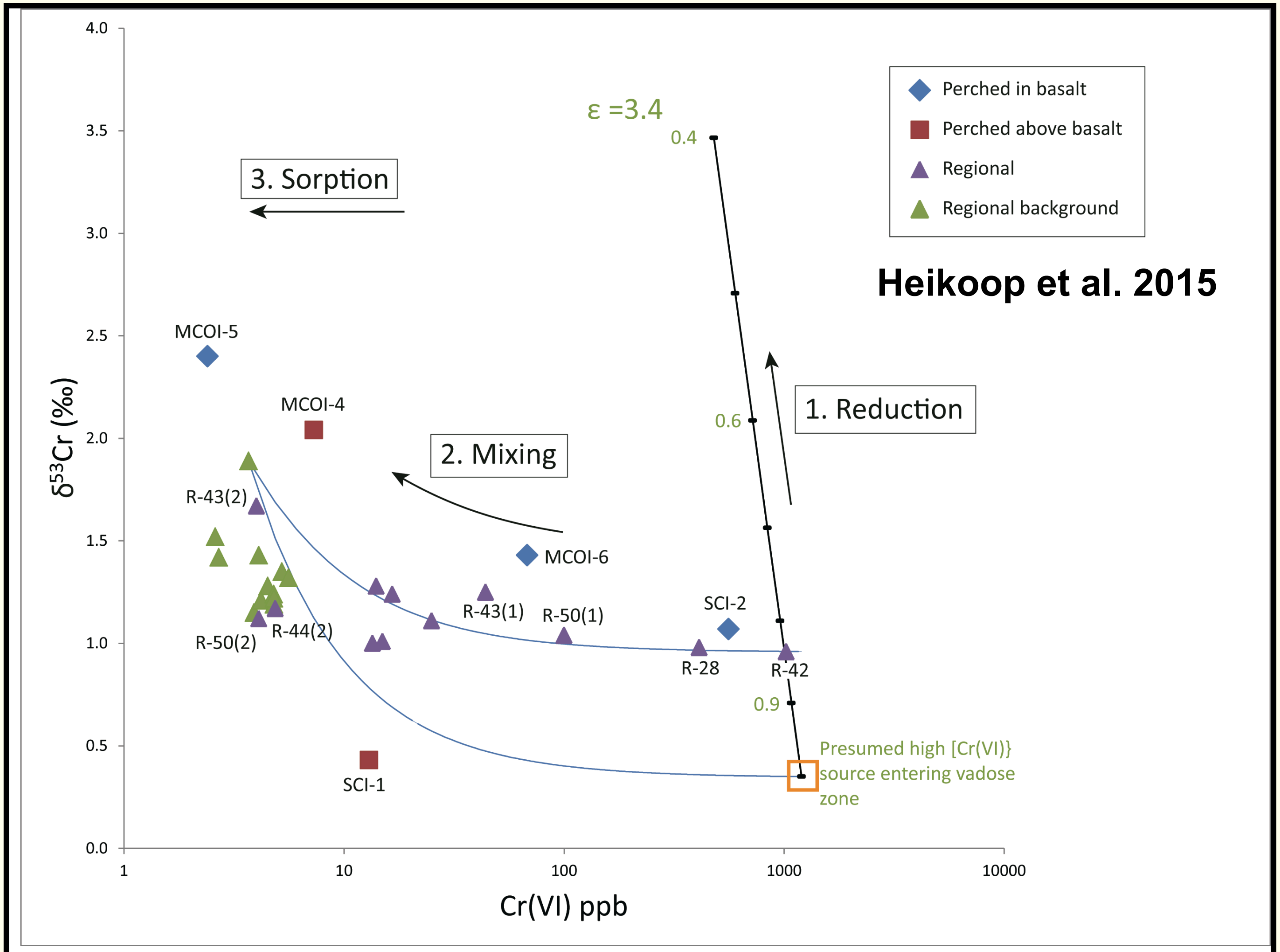
^{52}Cr has an abundance of 83.79 percent in nature.

^{53}Cr has an abundance of 9.50 percent in nature.

Residual chromate becomes enriched in ^{53}Cr as Cr(VI) reduces to Cr(III), precipitating as $Cr(OH)_3$.

Solid $Cr(OH)_3$ becomes enriched in ^{52}Cr during precipitation.

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



Heikoop et al. 2015

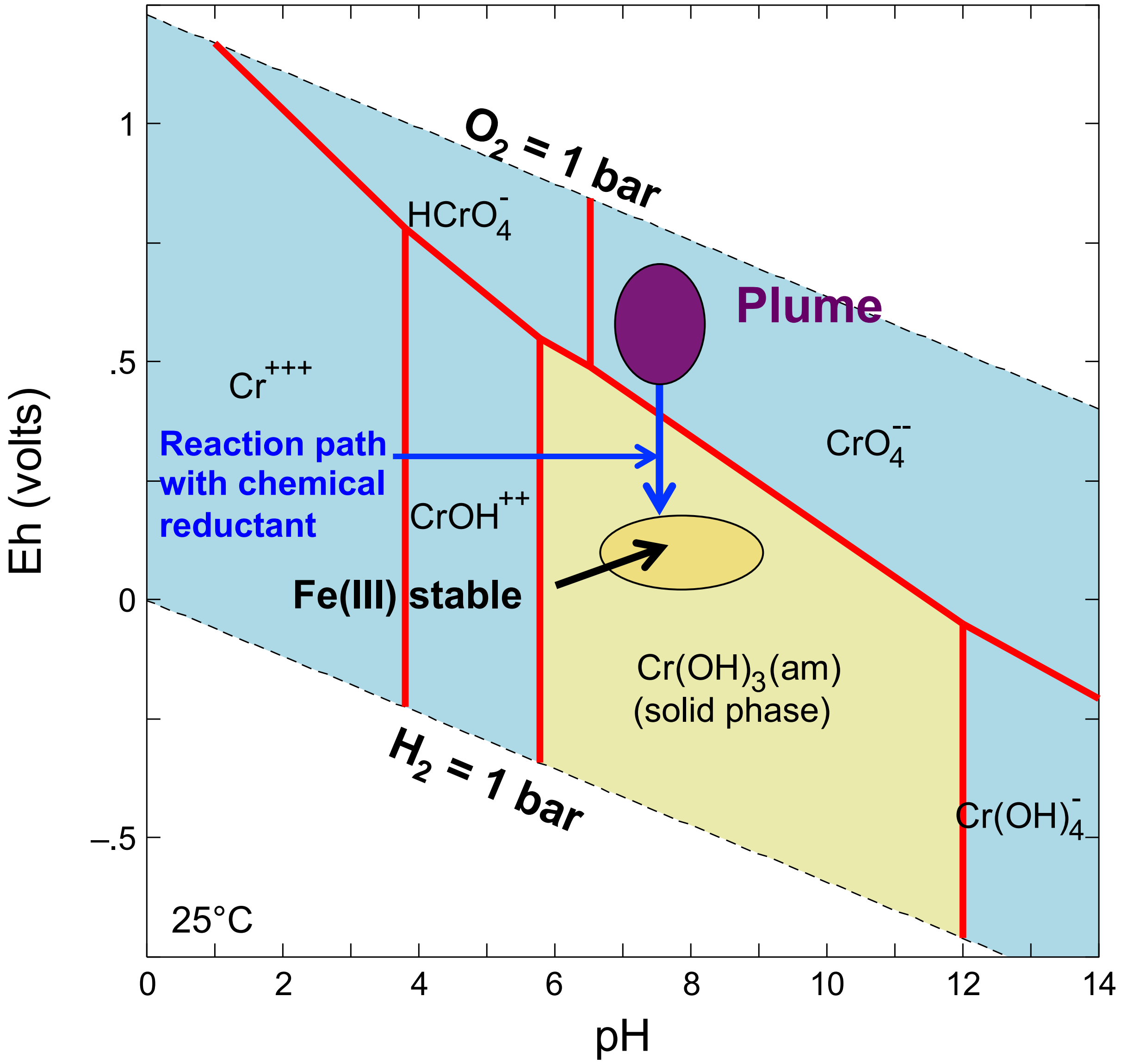
Figure 3

Remediation Options for Chromium in Soil and Aquifer Systems

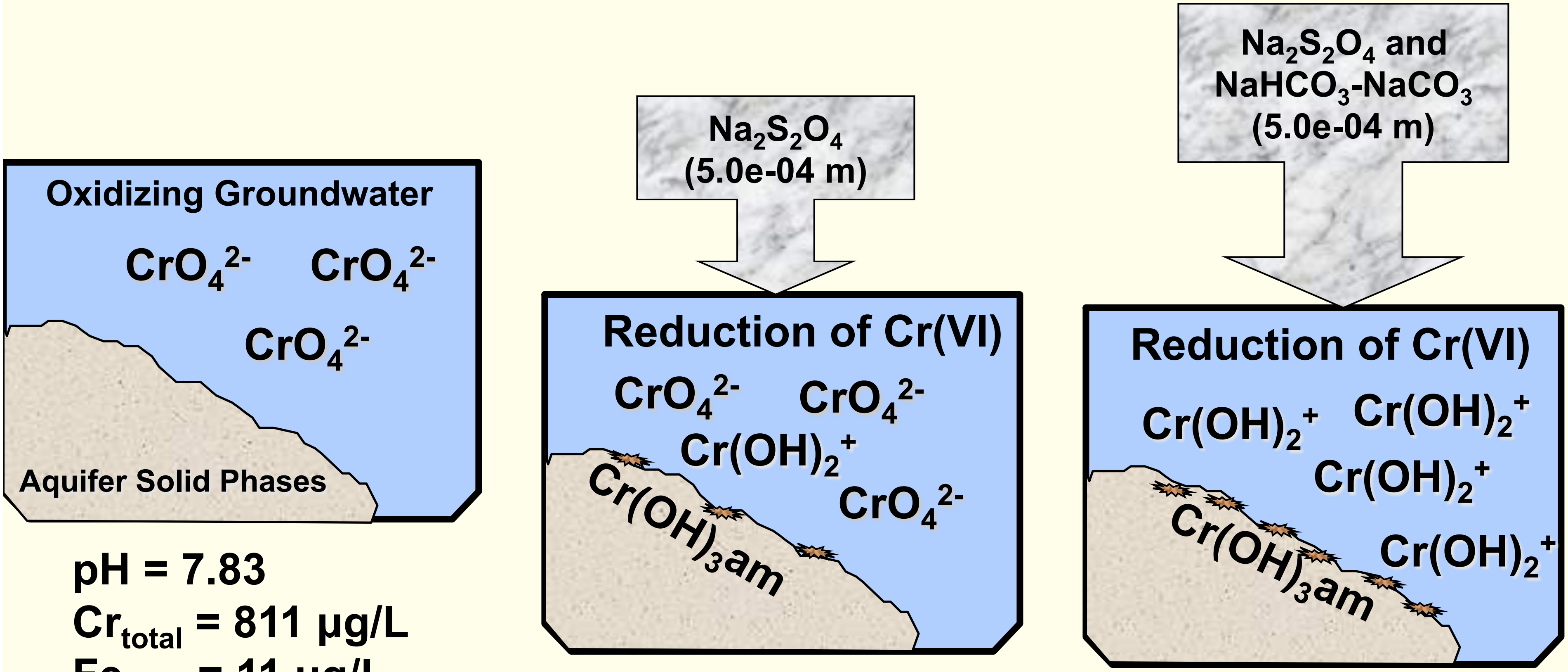
Physical	Ion Exchange-Adsorption	*In Situ* Chemical Reduction-Precipitation
Pump and Treat [Cr(VI)]	Anion, Cr(VI): $HCrO_4^-$, CrO_4^{2-}, $Cr_2O_7^{2-}$, $Cr(OH)_4^-$	CaS_5, HRC, Fe(0), wetlands, humic and fulvic acids, microbial, $Na_2S_2O_4$, $NaHSO_3$, $CaHSO_3$, Na_2S, Fe(II), GAC, electrolysis, 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.

Eh-pH Diagram for Part of the Cr-O-H System at 25°C and 1 Bar, Total Dissolved Cr = $10^{-4.74}$ Molal



Reduction of Chromate by Sodium Dithionite ($Na_2S_2O_4$)



Oxidizing Groundwater

CrO_4^{2-} CrO_4^{2-}

CrO_4^{2-}

Aquifer Solid Phases

pH = 7.83
Cr_{total} = 811 µg/L
Fe_{total} = 11 µg/L

✷ **$Cr(OH)_3am$**

$Na_2S_2O_4$
(5.0e-04 m)

Reduction of Cr(VI)

CrO_4^{2-} CrO_4^{2-}

$Cr(OH)_2^+$

CrO_4^{2-}

$Cr(OH)_3am$

pH = 5.44
Cr_{total} = 440 µg/L
$Cr(OH)_3am$ = 371 µg/L

$Na_2S_2O_4$ and
$NaHCO_3$-$NaCO_3$
(5.0e-04 m)

Reduction of Cr(VI)

$Cr(OH)_2^+$ $Cr(OH)_2^+$

$Cr(OH)_2^+$

$Cr(OH)_2^+$

$Cr(OH)_3am$

pH = 7.72
Cr_{total} = 0.26 µg/L
$Cr(OH)_3am$ = 811 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.

Summary and Conclusions

- **Natural attenuation of chromium(IV) is not an effective process taking place in the regional aquifer system.**
- **Successful *in situ* aquifer remediation of chromium in the regional aquifer requires complete understanding of:**

  Nature and extent of contamination and

  Geochemical, biochemical, and hydrologic characteristics.
- **Chemical reductants, such as sodium dithionite, nano-zero valance iron, and calcium polysulfide, have been used at other chromium-contaminated sites to remediate groundwater.**

SUPPLEMENTAL MATERIAL

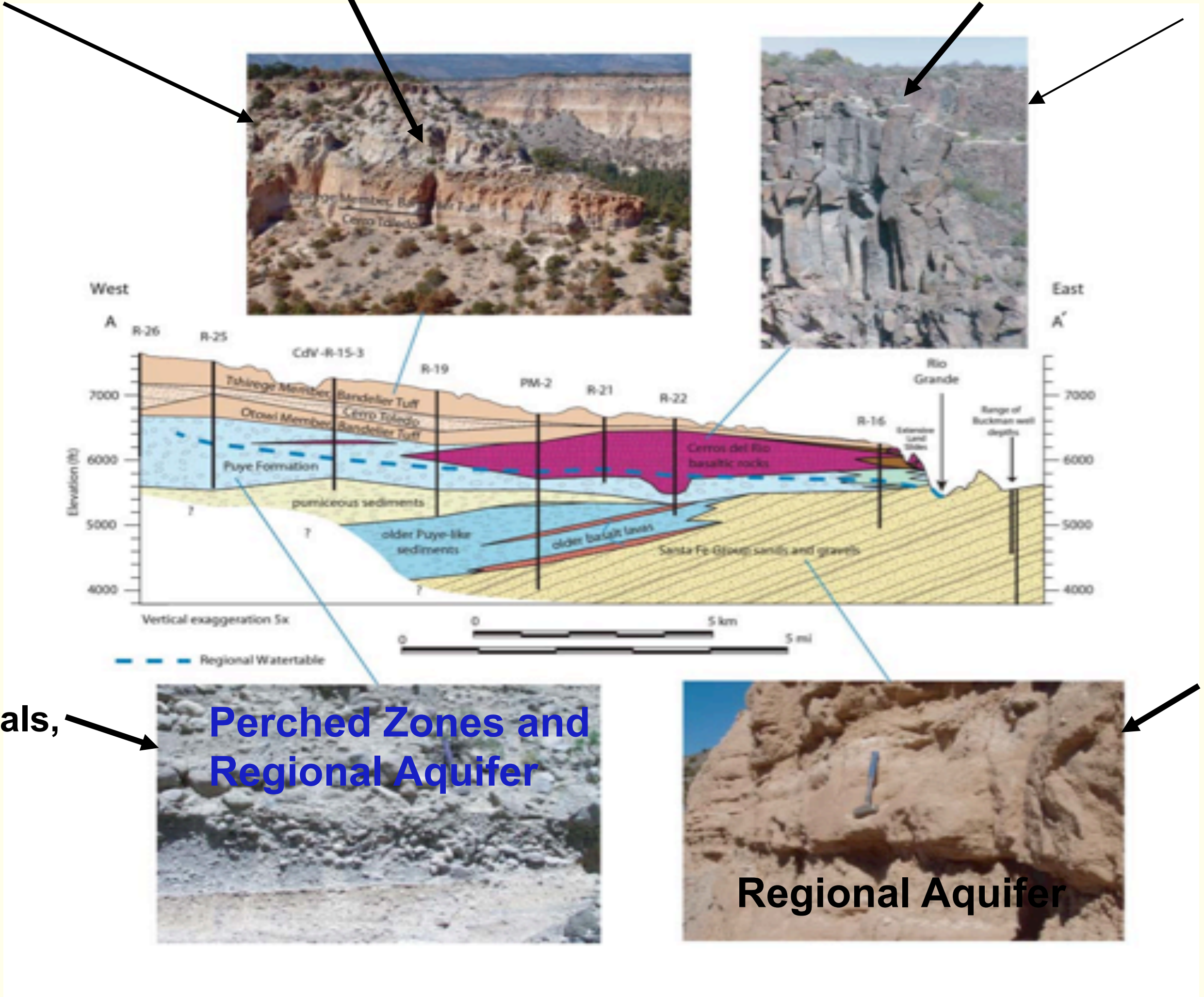
LANL Hydrostratigraphy and Reactive Solids

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

Perched Zones

Perched Zones and Regional Aquifer

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



clay minerals, $Fe(OH)_3$

Perched Zones and Regional Aquifer

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

Regional Aquifer

Sandia Canyon Wetland Dewatering Studies – *Can Cr(III) naturally convert to Cr(VI)?*

Under reducing conditions, Mn(II) and Cr(III) are stable within the active wetland.

8 locations – sediment and organic rich materials

Natural and oven drying

1, 2, 4, and 12 months

DI H_2O and treated sewage effluent

Cr(VI) ranged – 0.06 to 14.5 ppb

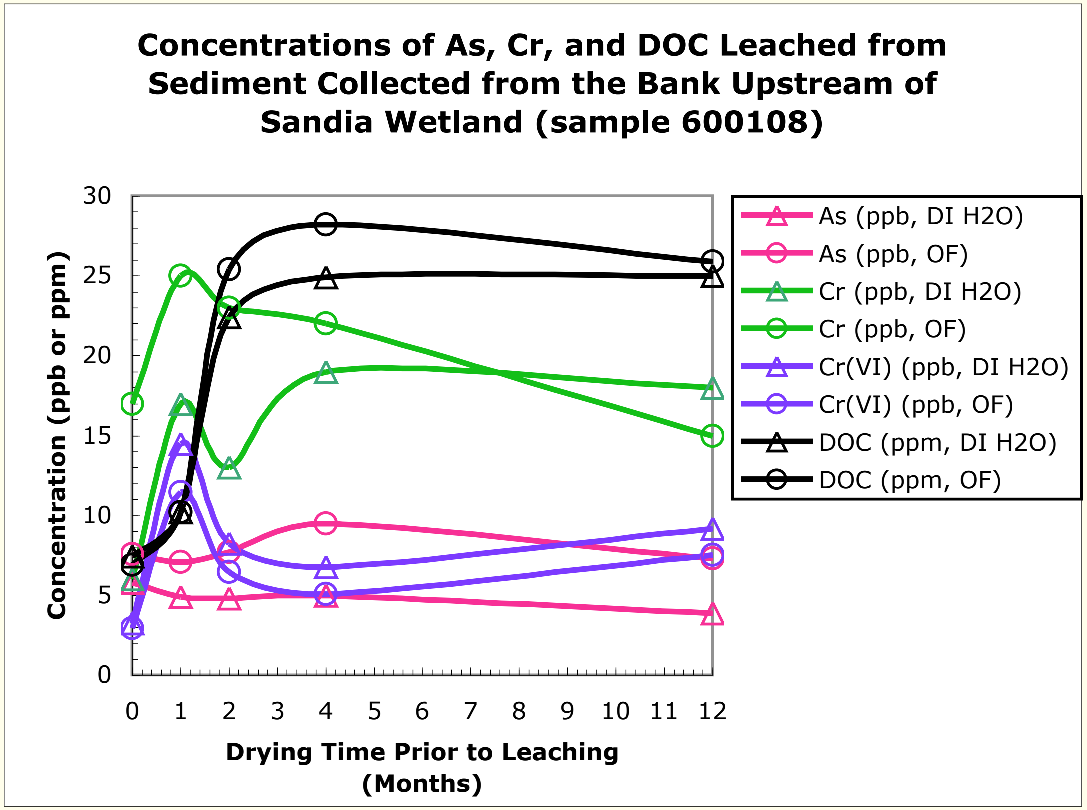
Analysis of Mn(IV) to Fe(II) to Cr(III) indicate stability of Cr(III)

Agrees with observed stable mass of Cr(III) in wetland 35 yr after release

Under oxidizing conditions Mn(II) will oxidize to Mn(IV). Mn(IV) is then available to *potentially* reoxidize Cr(III) to Cr(VI).

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

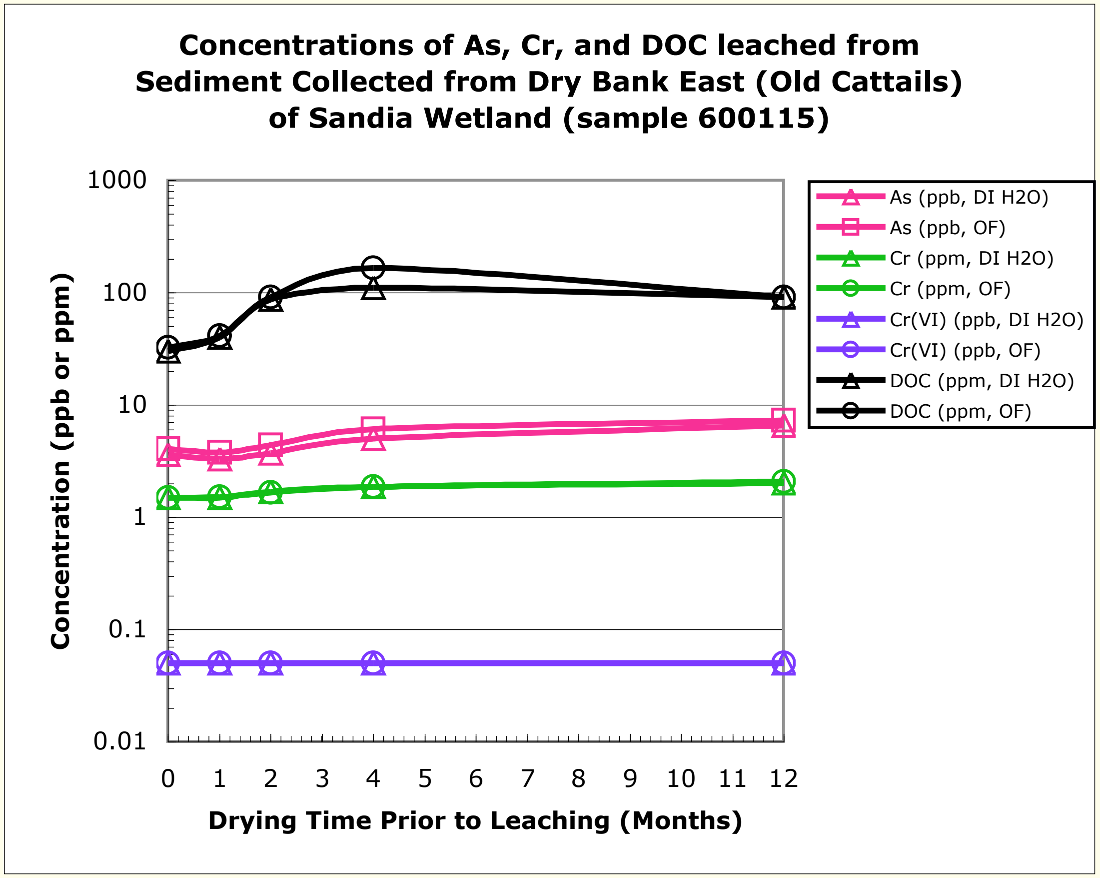
Results of Sandia Wetland Drying Experiments



Sample drying time (in months) prior to leaching versus concentrations of dissolved concentrations of arsenic (As) (ppb), total chromium (Cr) (ppb), hexavalent chromium [Cr(VI)], and dissolved organic carbon (DOC) (ppm) for sample 600108. Leaching solutions consisted of deionized water or treated sewage effluent.

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

Results of Sandia Wetland Drying Experiments



Sample drying time (in months) prior to leaching versus concentrations of dissolved concentrations of arsenic (As) (ppb), total chromium (Cr) (ppb), hexavalent chromium [Cr(VI)], and dissolved organic carbon (DOC) (ppm) for sample 600115. Leaching solutions consisted of deionized water or treated sewage effluent.

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

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

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

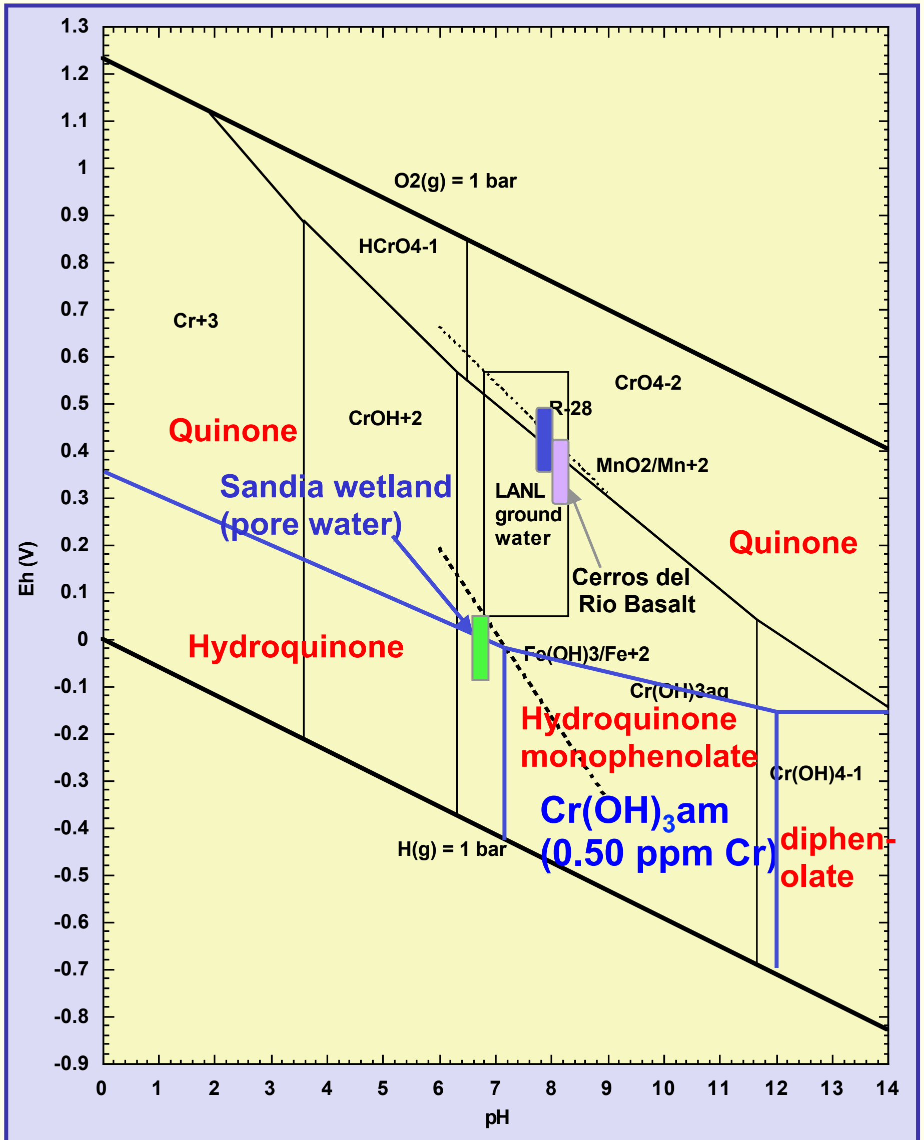
Cr Reduction:

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

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

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.

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

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 [≥3] moles Cr(VI)/g soil	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	Excellent	Excellent	Excellent	Excellent
moles Fe(II)/g soil [≥1] moles Mn(IV)/g soil	36.9	67.9	8.9	12.0
Potential for Cr(III) to remain reduced based on Fe(II)/Mn(IV) mole ratio	Excellent	Excellent	Excellent	Excellent

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

Attenuation Reactions of Chromium(III) in Dried Cattails at pH 3.80 (drying time = 12 months)

Chromium(III) associated with dried cattails = 3578 mg/kg.
Chromium(III) in effluent leachate = $10^{-4.39}$ moles/L (2.09 mg/L).

Effluent leachate is undersaturated with respect to $Cr(OH)_3$(am) with a saturation index (SI) of -3.10 (PHREEQC).

Cr(III) Adsorption onto Hydrous Ferric Oxide (PHREEQC)

$Fe^{s}OH + Cr^{3+} + H_2O - 2H^+ = Fe^{s}OOHCr^+$

3.72e-05 moles/L of hydrous ferric oxide (HFO) provides $10^{-6.92}$ moles of $Fe^{s}OOHCr^+$ adsorbing 6.31 μg/L Cr(III).

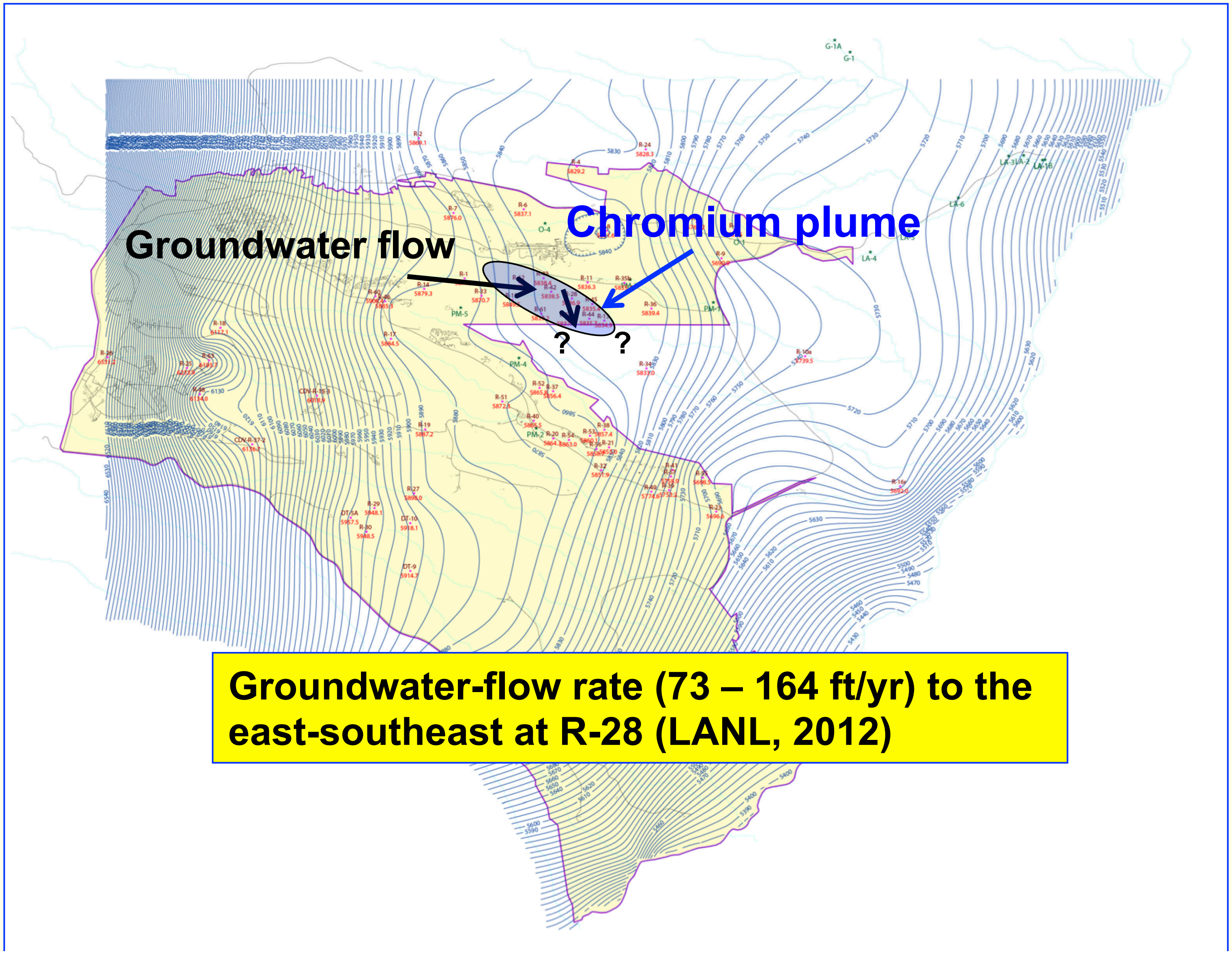
Cr(III) and Solid Organic Matter with Reactive Carboxalate

$R\text{-}COOH + Cr^{3+} = [R\text{-}COOCr]^{2+} + H^+$

Coprecipitation with HFO, H-Jarosite, and/or Na-Jarosite

Effluent leachate is saturated with respect to $H(Fe)_3(SO_4)_2(OH)_6$ (SI = 0.21) and $Na(Fe)_3(SO_4)_2(OH)_6$ (SI = 0.83).

Water Table Map for the Regional Aquifer, Los Alamos National Laboratory, NM (LANL 2012)



Groundwater-flow rate (73 – 164 ft/yr) to the east-southeast at R-28 (LANL, 2012)

HEXAVALENT CHROMIUM

The mass of chromate in soil can be estimated by performing leach tests in which exchangeable chromate is extracted with a tri-potassium phosphate solution (James and Bartlett, 1983) and then estimating the residual amount that remains in the form of solid barium chromate ($BaCrO_4$). The mass of chromium(VI) in soil(Cr(VI)tot) is:

$$Cr\ (VI)_{tot} = [CrO_4^{2-}] + 1000_{\rho b}[Cr(VI)_{exchangeable} + Cr(VI)_{BaCrO_4}]/\theta$$

where ρb is the bulk density of the soil (g/cm3) and θ is the porosity.

The mass of chromium (III) present in soil can be determined by performing selective extractions using dithionite-citrate-bicarbonate (DCB) by dissolving hydrous ferric oxide, ferrihydrite, aluminum hydroxide and unfortunately some of the chromium (VI) phases.

References

Bartlett, R.J. and James, B.R., 1988, Mobility and bioavailability of chromium in soils: *In* Chromium in the Natural and Human Environments, Vol. 20 (J.O.Nriagu and E. Nieboer, EDs.) pp. 267-307, John Wiley & Sons, New York.

Brady, P.V., Brady, M.V, and Borns, D.J., 1998, Natural Attenuation CERCLA, RBCA's, and the Future of Environmental Remediation: Lewis Pub., 245 p. Boca Raton, Florida.

Palmer, C.D. and Puls, R.W, 1994, Natural attenuation of hexavalent chromium in groundwater and soils: Groundwater Issue.

ELECTRON DONORS FOR REDUCING HEXAVALENT CHROMIUM

The aqueous electron donors are probably less important than solid phase electron donors because a contaminant plume displaces native or existing groundwater and that diffusion is a slow process.

Palmer and Puls (1994) calculate that less than 1 percent of the reducing capacity comes from the redox-sensitive solutes and over 99 percent comes from the redox-sensitive solid phase(s).

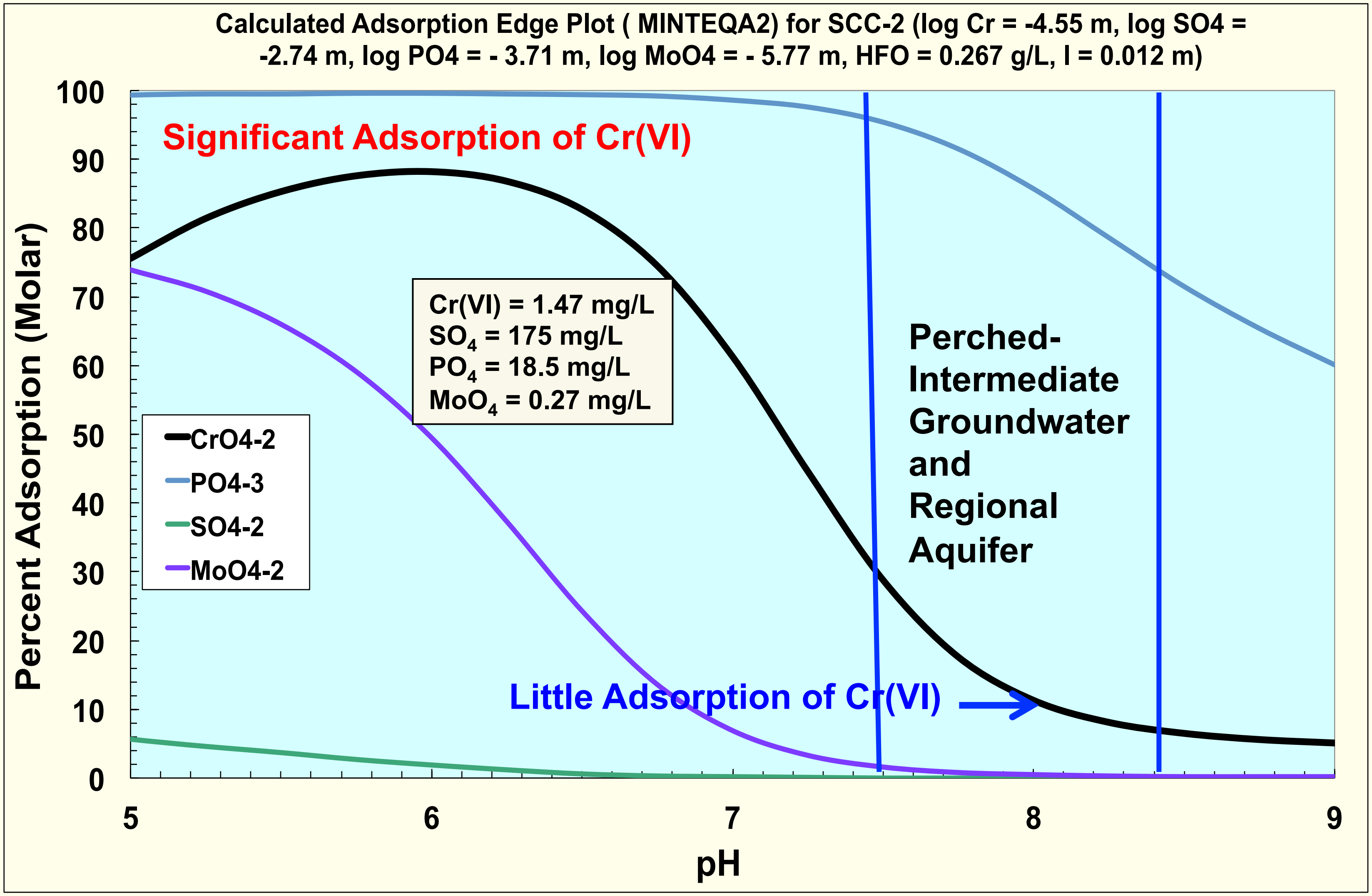
Criteria for Natural Attenuation of Chromium (EPA)

- **Natural attenuation of chromium in aquifer systems is supported by:**
- **Decreasing concentrations of chromium(VI) over time and distance;**
- **Decreasing volume of contaminated aquifer material over time;**
- **An abundance of reactive electron donors (reducing agents), required especially for Cr(VI) reduction, and electron acceptors (oxidizing agents);**

Criteria for Natural Attenuation of Chromium (EPA)

- **An abundance of strong adsorption sites present on mineral surfaces to allow for irreversible or weak desorption;**
- **Rapid kinetics enhancing mineral precipitation with slow dissolution rates;**
- **A sufficiently long groundwater-residence time to allow for adsorption, and precipitation processes to take place within a reasonable time frame; and**
- **Achieving contaminant concentrations at or below regulatory standards within a reasonable time frame.**

Calculated Adsorption Edge Plot Using MINTEQA2 for the Unsaturated Zone, Sandia Canyon, New Mexico



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)

Significant Adsorption of Cr(VI)

Cr(VI) = 1.47 mg/L
SO_4 = 175 mg/L
PO_4 = 18.5 mg/L
MoO_4 = 0.27 mg/L

Perched-Intermediate Groundwater and Regional Aquifer

Little Adsorption of Cr(VI)

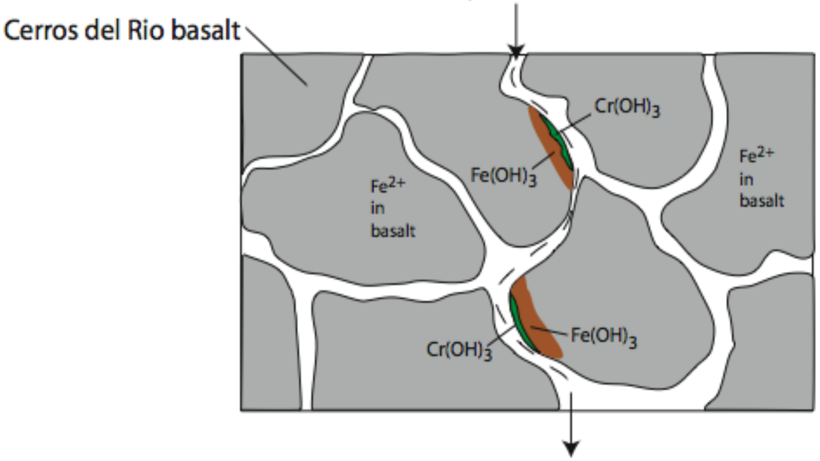
Outcrop of Cerros del Rio Basalt

Oxidation of basalt glass producing iron oxides may provide adsorption sites for chromate

Geochemical Conceptual Model for Chromium in the Cerros del Rio Basalt, Perched Zones

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)]



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

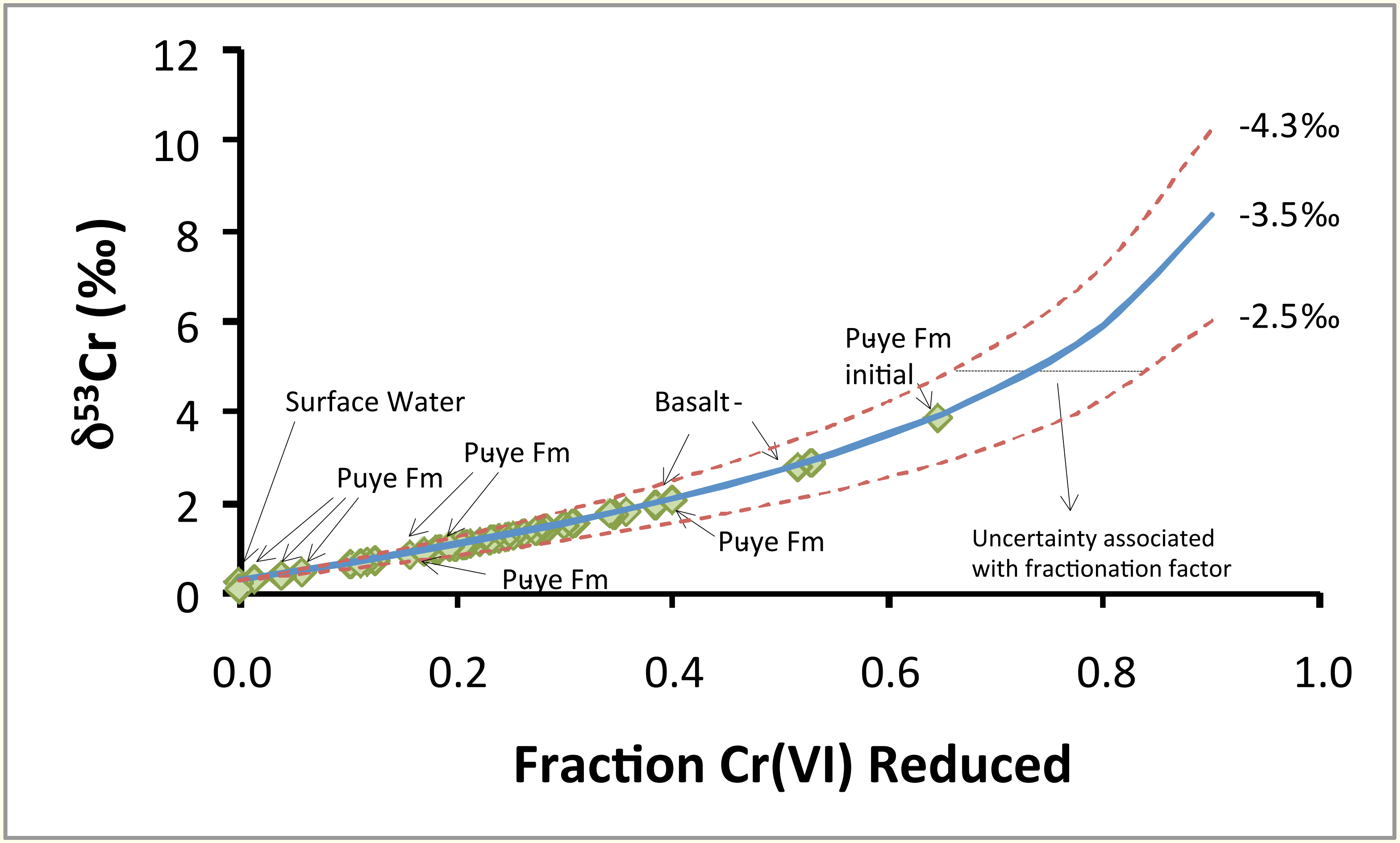
Reduction of Cr(VI) is followed by precipitation of Cr(III) [as Cr(OH)$_3$]

Output Cr(VI) at lower concentrations
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)

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



Source: Heikoop and Longmire, 2009

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.

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

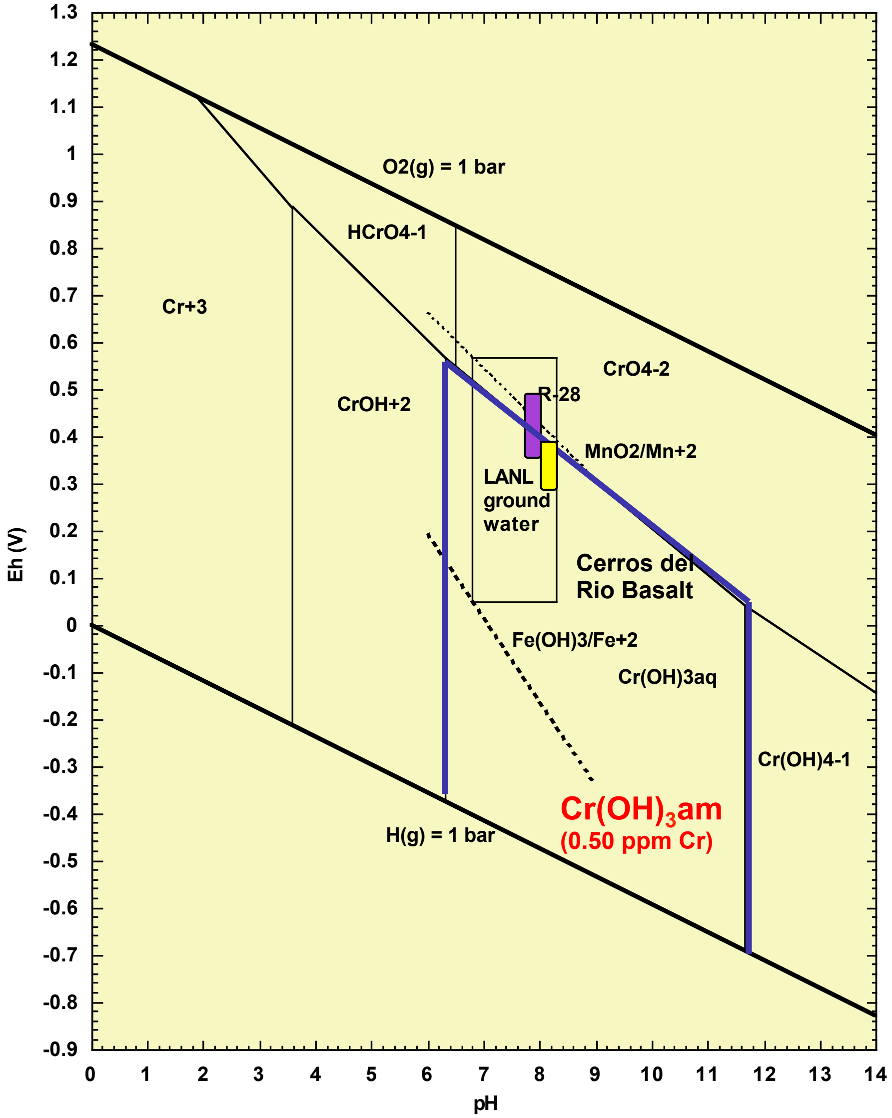
$Cr(OH)_3(am) + 3MnO_2(s) + H_2O = CrO_4^{2-} + 3MnOOH(s) + 2H^+$

Cr Reduction:

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

Dissolved Fe(II) and organic carbon

Solid organic matter

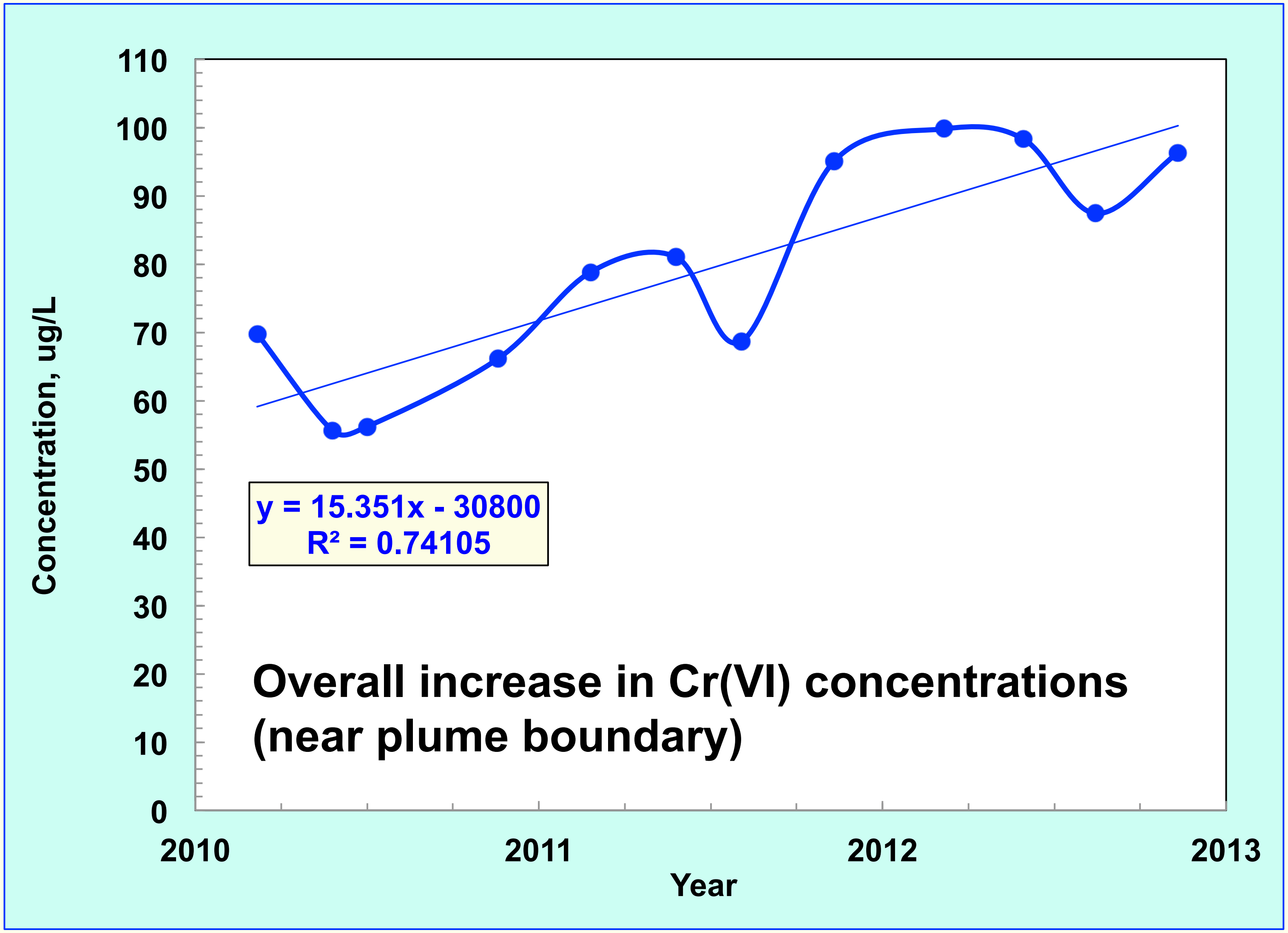


Eh-pH diagram for part of the Cr-Mn-Fe-O-H system at 25C and 1 bar. Log concentrations of total dissolved Fe and Mn = -4.75 and -4.74 molal, respectively.

Median Background Solute 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
SiO_2	1.16	69.55
NO_3(N)	0.04	0.54
Cr	5.87e-05	0.00305

Dissolved Concentrations of Chromium at Regional Aquifer Well R-50 Screen 1, Los Alamos, New Mexico



y = 15.351x - 30800
$R^2 = 0.74105$

Overall increase in Cr(VI) concentrations
(near plume boundary)

Plume Mapping- Methods

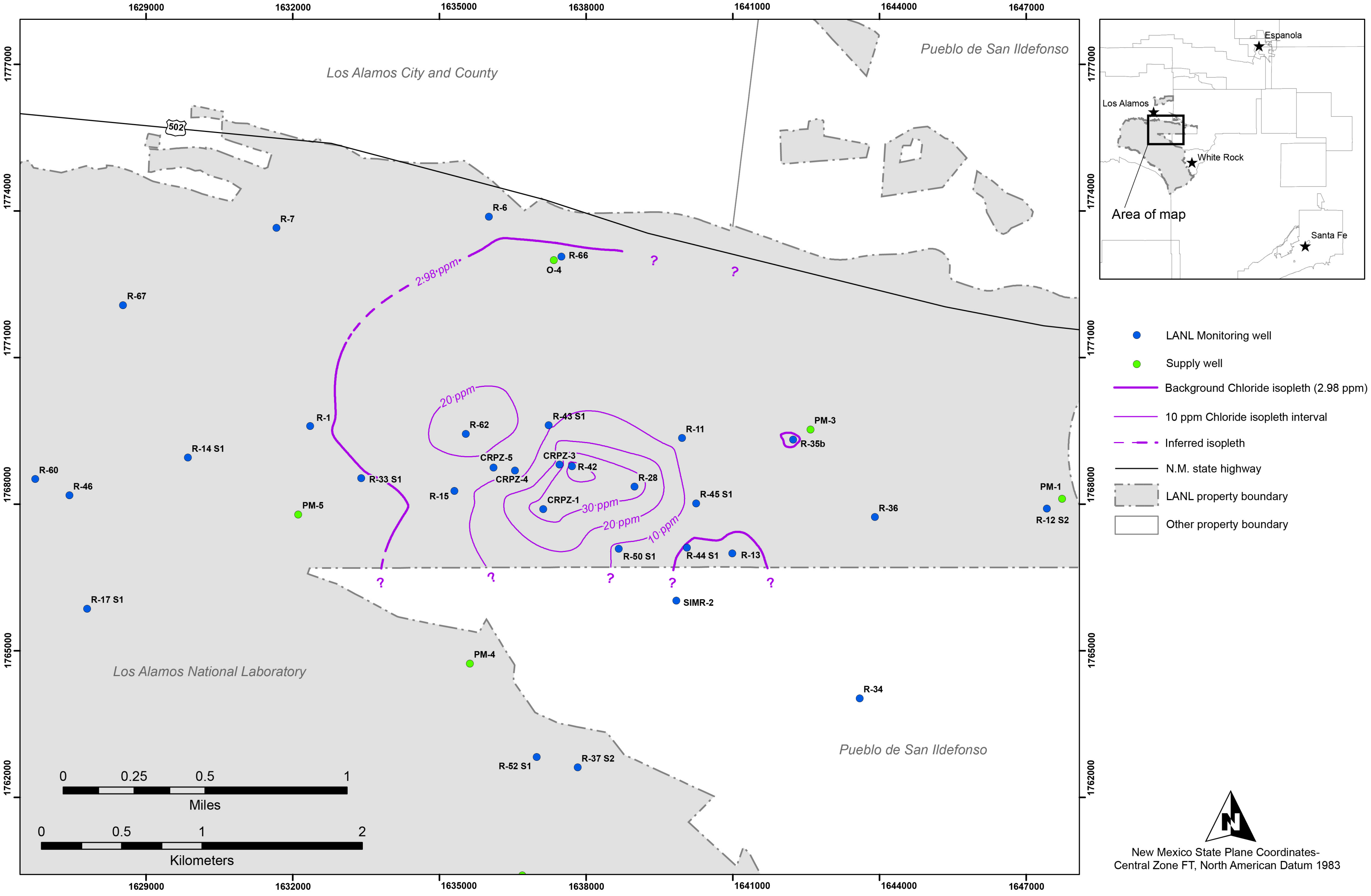
Targeted constituents: Cr, SO_4, NO_3, Cl, and ClO_4

Simple, two-dimensional visualizations created using a nearest neighbor interpolation (ArcMap 10.2, spatial analyst toolbox)

Input Data:

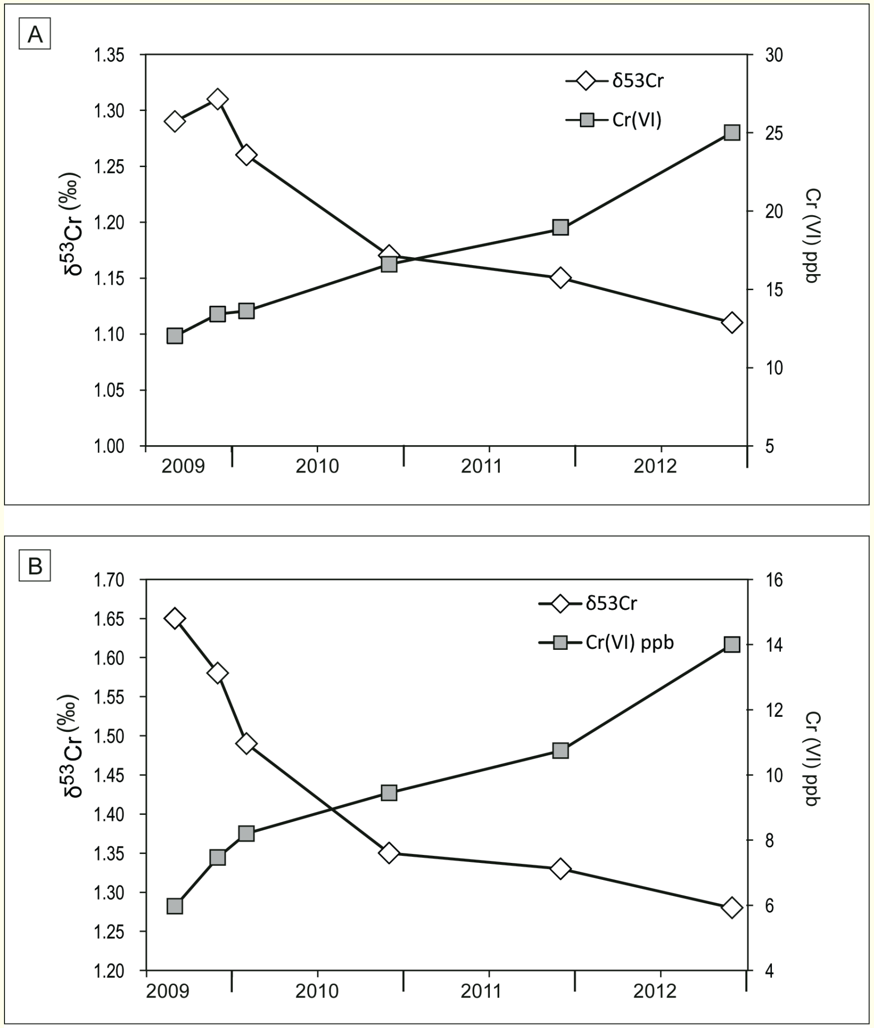
- 33 LANL monitoring wells, screened in top 50 ft of regional aquifer
- supply well data not used in interpolation
- most recent OR best data used
- NMED and LANL data
- most data available though Intellus (intellusnmdata.com)

Concentrations of Chloride in the Regional Aquifer, LANL



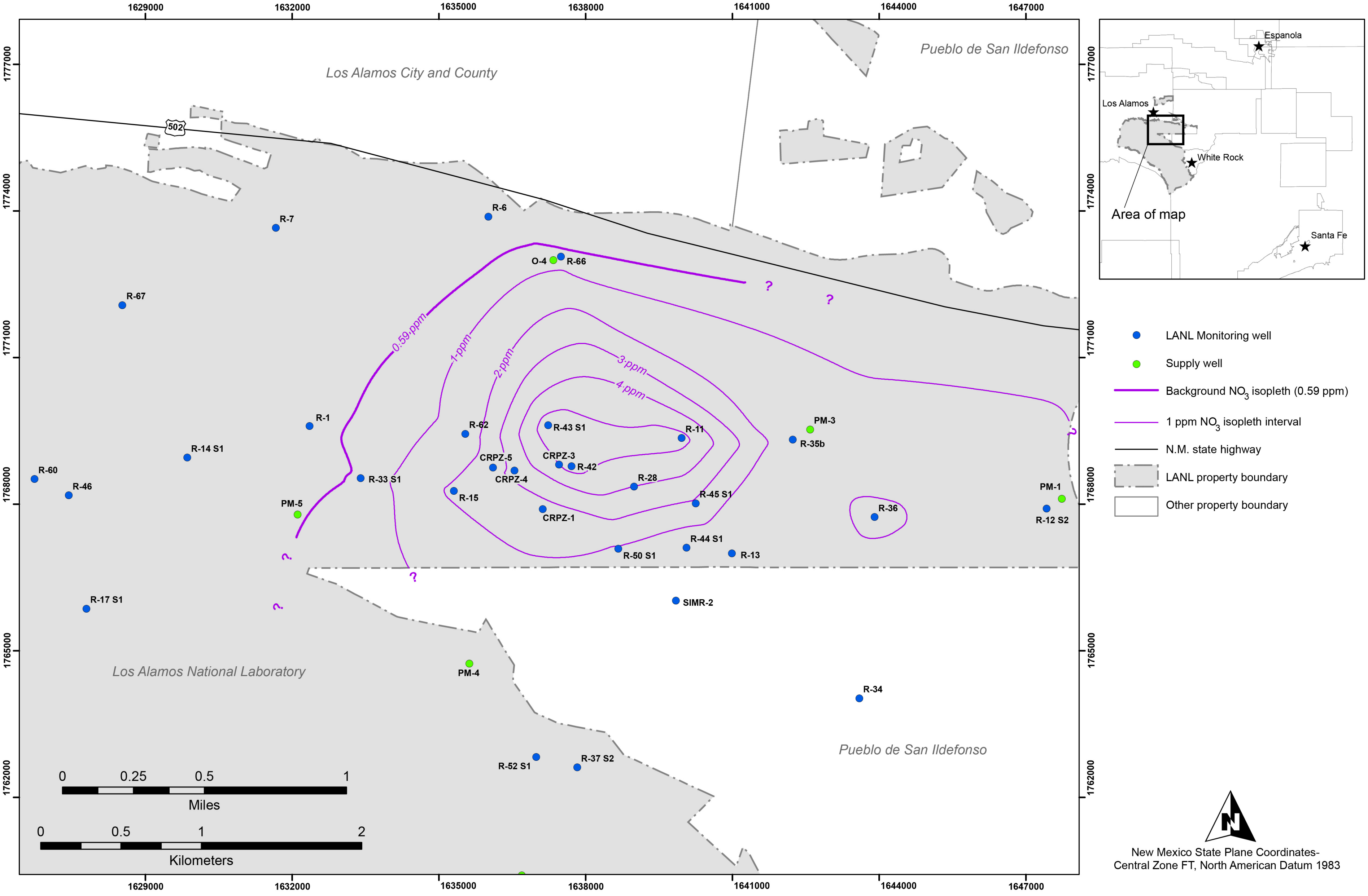
New Mexico State Plane Coordinates-
Central Zone FT, North American Datum 1983

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

Concentrations of Nitrate-Nitrite-N in the Regional Aquifer, LANL



Input Data for Groundwater Plume Map of Chloride, LANL

Location	Sample ID	Date	Parameter	Result	Units	Analytical Method
CRPZ-1	CrCH1-16-110478	02/08/2016	Chloride	36.548	mg/L	EPA:300.0
CRPZ-3	CRCH3-15-102169	07/13/2015	Chloride	22.501	mg/L	EPA:300.0
CRPZ-4	CRCH4-15-102175	07/08/2015	Chloride	3.0253	mg/L	EPA:300.0
CRPZ-5	CRCH5-15-102181	07/15/2015	Chloride	7.8321	mg/L	EPA:300.0
R-1	CAMO-16-106117	11/20/2015	Chloride	1.89	mg/L	EPA:300.0
R-11	CASA-16-106253	11/11/2015	Chloride	4.78	mg/L	EPA:300.0
R-12 S2	CASA-15-102649	08/18/2015	Chloride	6.96	mg/L	EPA:300.0
R-13	CAMO-16-106118	11/10/2015	Chloride	2.42	mg/L	EPA:300.0
R-14 S1	CAMO-16-106119	11/19/2015	Chloride	1.68	mg/L	EPA:300.0
R-15	CAMO-16-106120	11/20/2015	Chloride	4.07	mg/L	EPA:300.0
R-17 S1	CAPA-15-93474	04/20/2015	Chloride	1.91	mg/L	EPA:300.0
R-28	CAMO-16-106121	11/16/2015	Chloride	36.3	mg/L	EPA:300.0
R-33 S1	CAMO-16-106122	11/12/2015	Chloride	2.3	mg/L	EPA:300.0
R-34	CAMO-16-106124	11/24/2015	Chloride	2.44	mg/L	EPA:300.0
R-35b	CASA-16-106255	11/06/2015	Chloride	2.84	mg/L	EPA:300.0
R-36	CASA-16-106256	11/17/2015	Chloride	6.29	mg/L	EPA:300.0
R-37 S2	CAMO-16-105772	10/28/2015	Chloride	2.41	mg/L	EPA:300.0
R-42	CAMO-16-106125	11/16/2015	Chloride	45.7	mg/L	EPA:300.0
R-43 S1	CASA-16-106257	11/18/2015	Chloride	8.35	mg/L	EPA:300.0
R-44 S1	CAMO-16-106126	11/12/2015	Chloride	2.41	mg/L	EPA:300.0
R-45 S1	CAMO-16-106128	11/11/2015	Chloride	4.91	mg/L	EPA:300.0
R-46	CAMO-16-106130	11/18/2015	Chloride	1.72	mg/L	EPA:300.0
R-50 S1	CAMO-16-106131	11/09/2015	Chloride	7.26	mg/L	EPA:300.0
R-52 S1	CAPA-16-105615	10/21/2015	Chloride	2.61	mg/L	EPA:300.0
R-6	CALA-15-104011	09/09/2015	Chloride	1.89	mg/L	EPA:300.0
R-60	CAMO-16-106133	11/17/2015	Chloride	1.84	mg/L	EPA:300.0
R-62	Cr-R62-14-84669	07/30/2014	Chloride	14.126	mg/L	EPA:300.0
R-66	CALA-15-104013	09/14/2015	Chloride	3.76	mg/L	EPA:300.0
R-67	CASA-16-106065	12/03/2015	Chloride	2.31	mg/L	EPA:300.0
R-9	CALA-15-104017	09/16/2015	Chloride	6.77	mg/L	EPA:300.0
SIMR-2	CASA-16-106262	11/24/2015	Chloride	2.22	mg/L	EPA:300.0

Input Data for Groundwater Plume Map of Chromium, LANL

Location	Sample ID	Date	Parameter	Result	Units	Analytical Method
CRPZ-1	HACH NMED	2/10/2016	Chromium	470	ug/L	SW-846:6020
CRPZ-3	LANL	5/7/2015	Chromium	332	ug/L	SW-846:6021
CRPZ-4	LANL	4/30/2015	Chromium	7.65	ug/L	SW-846:6022
CRPZ-5	LANL	5/15/2015	Chromium	247	ug/L	SW-846:6023
R-1	R-1-11-10-14-HRMS	11/10/2014	Chromium	5.81	ug/L	EPA:200.8M
R-11	R-11-8-7-15-HRMS	08/07/2015	Chromium	19.5	ug/L	EPA:200.8M
R-12 S2	R-12 S2-7-22-13-HRMS	7/25/2013	Chromium	0.801	ug/L	EPA:200.8M
R-13	R-13-8-11-15-HRMS	08/11/2015	Chromium	3.62	ug/L	EPA:200.8M
R-14 S1	R-14-5-6-14-HRMS	5/6/2014	Chromium	5.21	ug/L	EPA:200.8M
R-15	R-15-8-13-15-HRMS	08/13/2015	Chromium	11.4	ug/L	EPA:200.8M
R-17 S1	R-17-SCR 1-5-2-12-HRM	5/2/2012	Chromium	2.04	ug/L	EPA:200.8M
R-28	R-28-8-8-HRM	08/08/2012	Chromium	410	ug/L	EPA:200.8M
R-33 S1	R-33 S1-8-6-15-HRMS	08/06/2015	Chromium	4.66	ug/L	EPA:200.8M
R-34	R-34-05-15-13-HRMS	5/15/2013	Chromium	4.5	ug/L	EPA:200.8M
R-35a	R-35A-8-10-15-HRMS	08/10/2015	Chromium	3.94	ug/L	EPA:200.8M
R-35b	R-35B-8-4-15-HRMS	08/04/2015	Chromium	4.33	ug/L	EPA:200.8M
R-36	R-36-8-7-15-HRMS	08/07/2015	Chromium	5.01	ug/L	EPA:200.8M
R-37 S2	R-37 S2-10-22-12-HRM	10/22/2012	Chromium	2.69	ug/L	EPA:200.8M
R-42	R-42-5-8-14-HRMS	05/08/2014	Chromium	812	ug/L	EPA:200.8M
R-43 S1	R-43 S1-11-21-14-HRMS	11/21/2014	Chromium	119	ug/L	EPA:200.8M
R-44 S1	R-44 S1-8-6-15-HRMS	08/06/2015	Chromium	15.4	ug/L	EPA:200.8M
R-45 S1	R-45 S1-8-5-15-HRMS	08/05/2015	Chromium	33.9	ug/L	EPA:200.8M
R-46	R-46-5-9-14-HRMS	5/9/2014	Chromium	5.07	ug/L	EPA:200.8M
R-50 S1	R-50 S1-8-5-15-HRMS	08/05/2015	Chromium	104	ug/L	EPA:200.8M
R-52 S1	R-52 S1-10-16-12-HRM	10/21/2015	Chromium	2.65	ug/L	EPA:200.8M
R-6	R-6-8-7-13-HRMS	8/7/2013	Chromium	4.45	ug/L	EPA:200.8M
R-60	R-60-5-12-14-HRMS	5/12/2014	Chromium	4.9	ug/L	EPA:200.8M
R-62	HACH NMED, 20 CV	06/26/2014	Chromium	270	ug/L	EPA:200.8M
R-66	R-66-8-16-13-HRMS	8/16/2013	Chromium	2.9	ug/L	EPA:200.8M
R-67	CASA-16-106065	12/3/2015	Chromium	7.11	ug/L	SW-846:6020
R-7	CALA-10-9190	1/14/2010	Chromium	5.0608	ug/L	SW-846:6023
R-9	R-9-8-6-13-HRMS	8/6/2013	Chromium	3.04	ug/L	EPA:200.8M
SIMR-2	SIMR-2-10-23-15-HRMS	10/23/2015	Chromium	4.73	ug/L	EPA:200.8M

Input Data for Groundwater Plume Map of Nitrate-Nitrite-N, LANL

Location	Sample ID	Date	Parameter	Result	Units	Analytical Method
CRPZ-4	CrPZ-4-4-30-15-N	4/30/2015	Nitrate-Nitrite as Nitrogen	3.2	mg/L	EPA:353.2
R-1	CAMO-16-106117	11/20/2015	Nitrate-Nitrite as Nitrogen	0.346	mg/L	EPA:353.2
R-11	CASA-16-106253	11/11/2015	Nitrate-Nitrite as Nitrogen	5.42	mg/L	EPA:353.2
R-12 S2	CASA-15-102649	08/18/2015	Nitrate-Nitrite as Nitrogen	1.25	mg/L	EPA:353.2
R-13	CAMO-16-106118	11/10/2015	Nitrate-Nitrite as Nitrogen	0.737	mg/L	EPA:353.2
R-14 S1	CAMO-16-106119	11/19/2015	Nitrate-Nitrite as Nitrogen	0.354	mg/L	EPA:353.2
R-15	CAMO-16-106120	11/20/2015	Nitrate-Nitrite as Nitrogen	2.2	mg/L	EPA:353.2
R-17 S1	CAPA-15-93474	04/20/2015	Nitrate-Nitrite as Nitrogen	0.226	mg/L	EPA:353.2
R-28	CAMO-16-106121	11/16/2015	Nitrate-Nitrite as Nitrogen	3.97	mg/L	EPA:353.2
R-33 S1	CAMO-16-106122	11/12/2015	Nitrate-Nitrite as Nitrogen	0.522	mg/L	EPA:353.2
R-34	CAMO-15-102606	09/03/2015	Nitrate-Nitrite as Nitrogen	0.435	mg/L	EPA:353.2
R-35b	CASA-16-106255	11/06/2015	Nitrate-Nitrite as Nitrogen	1.23	mg/L	EPA:353.2
R-36	CASA-16-106256	11/17/2015	Nitrate-Nitrite as Nitrogen	2.29	mg/L	EPA:353.2
R-37 S2	CAMO-16-105772	10/28/2015	Nitrate-Nitrite as Nitrogen	0.605	mg/L	EPA:353.2
R-42	CAMO-16-106125	11/16/2015	Nitrate-Nitrite as Nitrogen	5.37	mg/L	EPA:353.2
R-43 S1	CASA-16-106257	11/18/2015	Nitrate-Nitrite as Nitrogen	5.61	mg/L	EPA:353.2
R-44 S1	CAMO-16-106126	11/12/2015	Nitrate-Nitrite as Nitrogen	1.14	mg/L	EPA:353.2
R-45 S1	CAMO-16-106128	11/11/2015	Nitrate-Nitrite as Nitrogen	2.86	mg/L	EPA:353.2
R-46	CAMO-16-106130	11/18/2015	Nitrate-Nitrite as Nitrogen	0.353	mg/L	EPA:353.2
R-50 S1	CAMO-16-106131	11/09/2015	Nitrate-Nitrite as Nitrogen	1.9	mg/L	EPA:353.2
R-52 S1	CAPA-16-105615	10/21/2015	Nitrate-Nitrite as Nitrogen	0.734	mg/L	EPA:353.2
R-6	CALA-15-104011	09/09/2015	Nitrate-Nitrite as Nitrogen	0.216	mg/L	EPA:353.2
R-60	CAMO-16-106133	11/17/2015	Nitrate-Nitrite as Nitrogen	0.388	mg/L	EPA:353.2
R-62	CAMO-16-106135	11/19/2015	Nitrate-Nitrite as Nitrogen	1.25	mg/L	EPA:353.2
R-66	CALA-15-104013	09/14/2015	Nitrate-Nitrite as Nitrogen	0.654	mg/L	EPA:353.2
R-67	CASA-16-106065	12/03/2015	Nitrate-Nitrite as Nitrogen	0.385	mg/L	EPA:353.2
R-9	CALA-15-104017	09/16/2015	Nitrate-Nitrite as Nitrogen	0.83	mg/L	EPA:353.2
SIMR-2	CASA-16-106066	10/23/2015	Nitrate-Nitrite as Nitrogen	0.706	mg/L	EPA:353.2

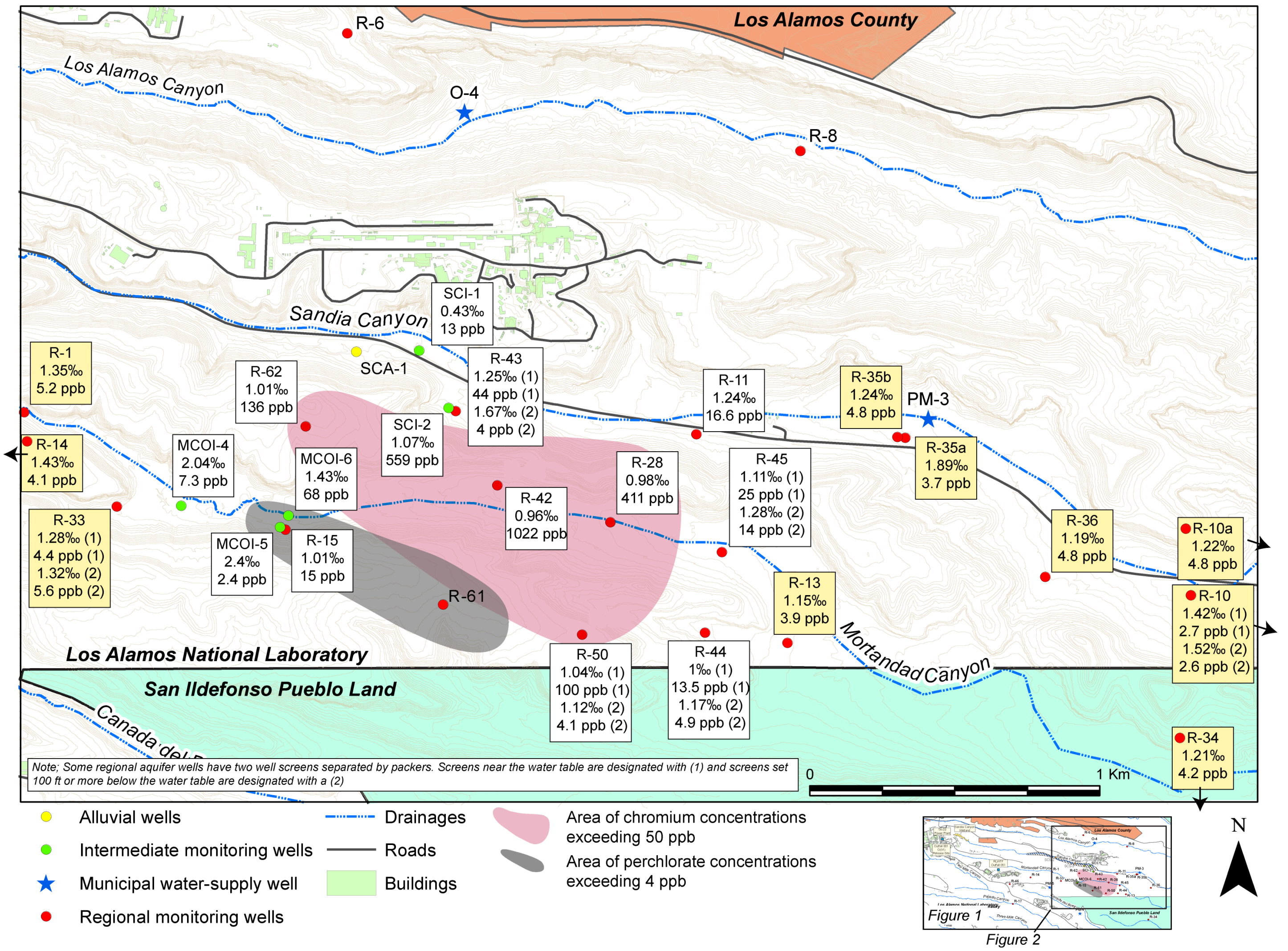
Input Data for Groundwater Plume Map of Perchlorate, LANL

Location	Sample ID	Date	Parameter	Result	Units	Analytical Method
CRPZ-1	CrCH1-15-102151	07/20/2015	Perchlorate	1.84	ug/L	SW-846:6850
CRPZ-3	CrCH3-15-102169	07/13/2015	Perchlorate	1.2	ug/L	SW-846:6850
CRPZ-4	CrCH4-15-102175	07/08/2015	Perchlorate	59.3	ug/L	SW-846:6850
CRPZ-5	CrCH5-15-102181	07/15/2015	Perchlorate	0.44	ug/L	SW-846:6850
R-1	CAMO-16-106117	11/20/2015	Perchlorate	0.373	ug/L	SW-846:6850
R-11	CASA-16-106253	11/11/2015	Perchlorate	0.868	ug/L	SW-846:6850
R-12 S2	CASA-15-102649	08/18/2015	Perchlorate	0.863	ug/L	SW-846:6850
R-13	CAMO-16-106118	11/10/2015	Perchlorate	0.419	ug/L	SW-846:6850
R-14 S1	CAMO-16-106119	11/19/2015	Perchlorate	0.296	ug/L	SW-846:6850
R-15	CAMO-16-106120	11/20/2015	Perchlorate	9.05	ug/L	SW-846:6850
R-17 S1	CAPA-15-93474	04/20/2015	Perchlorate	0.243	ug/L	SW-846:6850
R-28	CAMO-16-106121	11/16/2015	Perchlorate	1.09	ug/L	SW-846:6850
R-33 S1	CAMO-16-106122	11/12/2015	Perchlorate	0.393	ug/L	SW-846:6850
R-34	CASA-15-102619	09/03/2015	Perchlorate	0.2	ug/L	SW-846:6850
R-35a	CASA-16-106254	11/09/2015	Perchlorate	0.453	ug/L	SW-846:6850
R-35b	CASA-16-106255	11/06/2015	Perchlorate	0.626	ug/L	SW-846:6850
R-36	CASA-16-106256	11/17/2015	Perchlorate	1.61	ug/L	SW-846:6850
R-37 S2	CAMO-16-105772	10/28/2015	Perchlorate	0.393	ug/L	SW-846:6850
R-42	CAMO-16-106125	11/16/2015	Perchlorate	1.28	ug/L	SW-846:6850
R-43 S1	CASA-15-102653	08/19/2015	Perchlorate	1.02	ug/L	SW-846:6850
R-44 S1	CAMO-16-106126	11/12/2015	Perchlorate	0.441	ug/L	SW-846:6850
R-45 S1	CAMO-16-106128	11/11/2015	Perchlorate	0.633	ug/L	SW-846:6850
R-46	CAMO-16-106130	11/18/2015	Perchlorate	0.339	ug/L	SW-846:6850
R-50 S1	CAMO-16-106131	11/09/2015	Perchlorate	0.588	ug/L	SW-846:6850
R-52 S1	CAPA-16-105615	10/21/2015	Perchlorate	0.418	ug/L	SW-846:6850
R-6	CALA-15-104011	09/09/2015	Perchlorate	0.281	ug/L	SW-846:6850
R-60	CAMO-16-106133	11/17/2015	Perchlorate	0.35	ug/L	SW-846:6850
R-62	CAMO-16-106135	11/19/2015	Perchlorate	0.809	ug/L	SW-846:6850
R-66	CALA-15-104013	09/14/2015	Perchlorate	0.49	ug/L	SW-846:6850
R-67	CASA-16-106065	12/03/2015	Perchlorate	0.35	ug/L	SW-846:6850
R-7						
R-9	CALA-15-104017	09/16/2015	Perchlorate	1.05	ug/L	SW-846:6850
SIMR-2	CASA-16-106066	10/23/2015	Perchlorate	0.422	ug/L	SW-846:6850

Input Data for Groundwater Plume Map of Sulfate, LANL

Location	Sample ID	Date	Parameter	Result	Units	Analytical Method
CRPZ-1	CrCH1-15-102152	07/20/2015	Sulfate	51.75	mg/L	EPA:300.0
CRPZ-3	CRCH3-15-102169	07/13/2015	Sulfate	34.952	mg/L	EPA:300.0
CRPZ-4	CRCH4-15-102175	07/08/2015	Sulfate	5.6231	mg/L	EPA:300.0
CRPZ-5	CrCH5-15-97377	05/12/2015	Sulfate	8.1552	mg/L	EPA:300.0
R-1	CAMO-16-106117	11/20/2015	Sulfate	2.26	mg/L	EPA:300.0
R-11	CASA-16-106253	11/11/2015	Sulfate	11.7	mg/L	EPA:300.0
R-12 S2	CASA-15-102649	08/18/2015	Sulfate	8.54	mg/L	EPA:300.0
R-13	CAMO-16-106118	11/10/2015	Sulfate	3.16	mg/L	EPA:300.0
R-14 S1	CAMO-16-106119	11/19/2015	Sulfate	1.78	mg/L	EPA:300.0
R-15	CAMO-16-106120	11/20/2015	Sulfate	6.56	mg/L	EPA:300.0
R-17 S1	CAPA-15-93474	04/20/2015	Sulfate	1.72	mg/L	EPA:300.0
R-28	CAMO-16-106121	11/16/2015	Sulfate	51.6	mg/L	EPA:300.0
R-33 S1	CAMO-16-106122	11/12/2015	Sulfate	3.33	mg/L	EPA:300.0
R-34	CASA-15-102619	09/03/2015	Sulfate	0.4	mg/L	EPA:300.0
R-35a	CASA-16-106254	11/09/2015	Sulfate	5.46	mg/L	EPA:300.0
R-35b	CASA-16-106255	11/06/2015	Sulfate	3.5	mg/L	EPA:300.0
R-36	CASA-16-106256	11/17/2015	Sulfate	7.18	mg/L	EPA:300.0
R-37 S2	CAMO-16-105772	10/28/2015	Sulfate	2.97	mg/L	EPA:300.0
R-42	CAMO-16-106125	11/16/2015	Sulfate	77.1	mg/L	EPA:300.0
R-43 S1	CASA-16-106257	11/18/2015	Sulfate	16.2	mg/L	EPA:300.0
R-44 S1	CAMO-16-106126	11/12/2015	Sulfate	3.43	mg/L	EPA:300.0
R-45 S1	CAMO-16-106128	11/11/2015	Sulfate	7.61	mg/L	EPA:300.0
R-46	CAMO-16-106130	11/18/2015	Sulfate	1.84	mg/L	EPA:300.0
R-50 S1	CAMO-16-106131	11/09/2015	Sulfate	10.3	mg/L	EPA:300.0
R-52 S1	CAPA-16-105615	10/21/2015	Sulfate	3.72	mg/L	EPA:300.0
R-6	CALA-15-104011	09/09/2015	Sulfate	2.25	mg/L	EPA:300.0
R-60	CAMO-16-106133	11/17/2015	Sulfate	1.98	mg/L	EPA:300.0
R-62	CAMO-16-106135	11/19/2015	Sulfate	17.0	mg/L	EPA:300.0
R-66	CALA-15-104013	09/14/2015	Sulfate	3.52	mg/L	EPA:300.0
R-67	CASA-16-106065	12/03/2015	Sulfate	3.6	mg/L	EPA:300.0
R-7						
R-9	CALA-15-104017	09/16/2015	Sulfate	6.46	mg/L	EPA:300.0
SIMR-2	CASA-16-106066	10/23/2015	Sulfate	2.91	mg/L	EPA:300.0

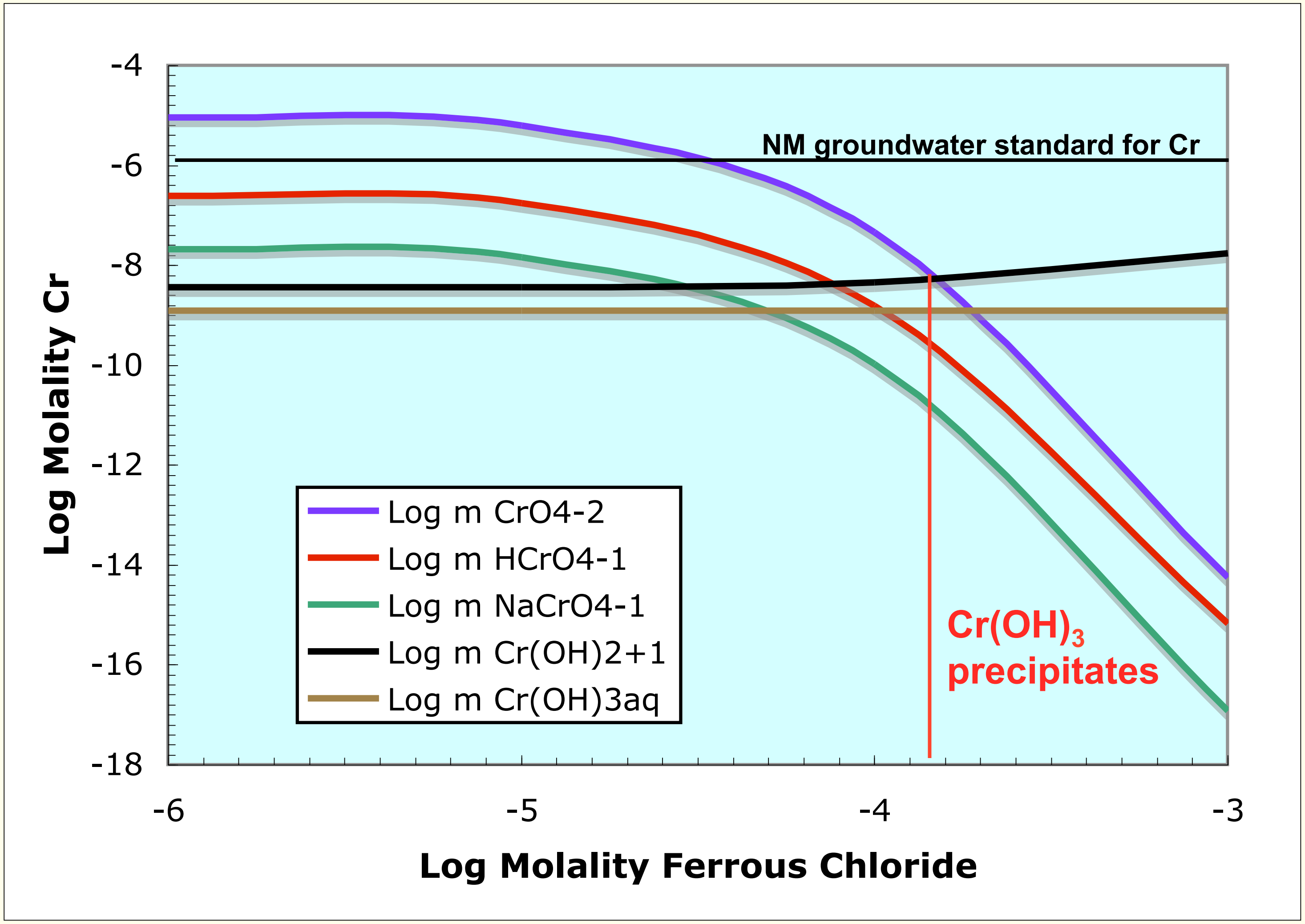
Distribution of Total Dissolved Chromium within the Regional Aquifer, Los Alamos National Laboratory, NM



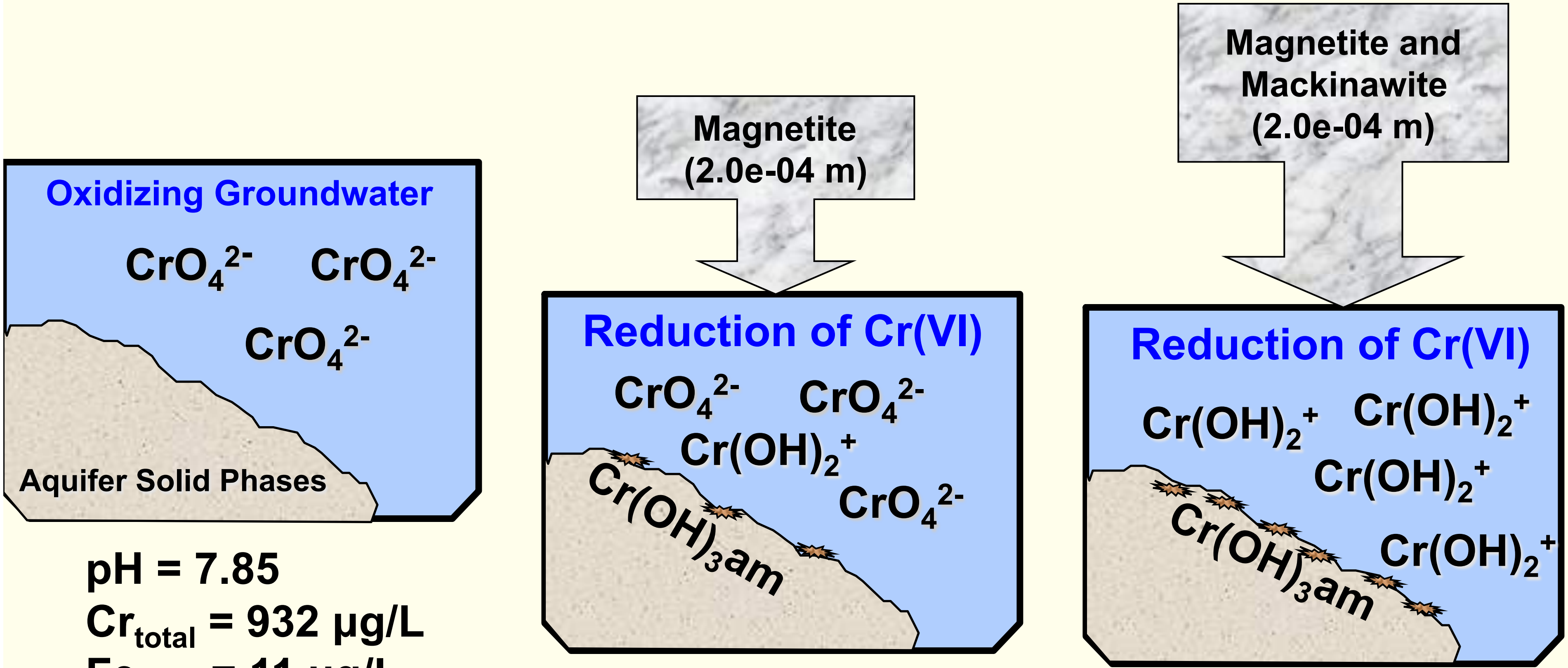
Note; Some regional aquifer wells have two well screens separated by packers. Screens near the water table are designated with (1) and screens set 100 ft or more below the water table are designated with a (2)

Figure 2

Results of Geochemical Modeling (PHREEQC2.2) Reacting R-28 Groundwater with Ferrous Chloride in Equilibrium with Calcite (NM groundwater standard for total Cr = 50 ppb or log m = -6.0)



Reduction of Chromate by Magnetite and/or Mackinawite



Oxidizing Groundwater

CrO_4^{2-} CrO_4^{2-}

CrO_4^{2-}

Aquifer Solid Phases

pH = 7.85

Cr_{total} = 932 µg/L

Fe_{total} = 11 µg/L

✷ **$Cr(OH)_3am$**

Magnetite
(2.0e-04 m)

Reduction of Cr(VI)

CrO_4^{2-} CrO_4^{2-}

$Cr(OH)_2^+$

CrO_4^{2-}

$Cr(OH)_3am$

pH = 7.72

Cr_{total} = 55 µg/L

Fe_{total} = < 5 µg/L

$Cr(OH)_3am$ = 877 µg/L

Magnetite and
Mackinawite
(2.0e-04 m)

Reduction of Cr(VI)

$Cr(OH)_2^+$ $Cr(OH)_2^+$

$Cr(OH)_2^+$

$Cr(OH)_2^+$

$Cr(OH)_3am$

pH = 7.02

Cr_{total} = 0.7 µg/L

Fe_{total} = < 5 µg/L

$Cr(OH)_3am$ = 932 µg/L

Summary and Conclusions

- **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.**
- **Experimental results agree with observed stable mass of Cr(III) in Sandia Canyon wetland 35 yr after Cr(VI) releases.**

SUMMARY AND CONCLUSIONS

- **Residual chromium (Cr) occurs in the unsaturated zone beneath Sandia and Mortandad Canyons, New Mexico.**
- **Transport of Cr(VI) occurs under relatively oxidizing and basic pH conditions within the vadose zone and regional aquifer.**
- **An unquantified fraction of anthropogenic Cr(VI) has reached the regional aquifer with dissolved concentrations up to 1200 μg/L.**