FATE AND TRANSPORT OF CHROMIUM IN THE REGIONAL AQUIFER, LOS ALAMOS, NEW MEXICO

BY

PATRICK LONGMIRE, Ph.D.

DEPARTMENT OF ENERGY -
OVERSIGHT BUREAU
NEW MEXICO ENVIRONMENT DEPARTMENT

1183 Diamond Dr., Suite B
Los Alamos, New Mexico 87544
Telephone: 505-661-2681
Email: patrick.longmire@state.nm.us

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I. Introduction

II. TA-3 Chromium Source

III. Direction and Rate of Groundwater Flow

IV. Distribution of Chromium in the Regional Aquifer

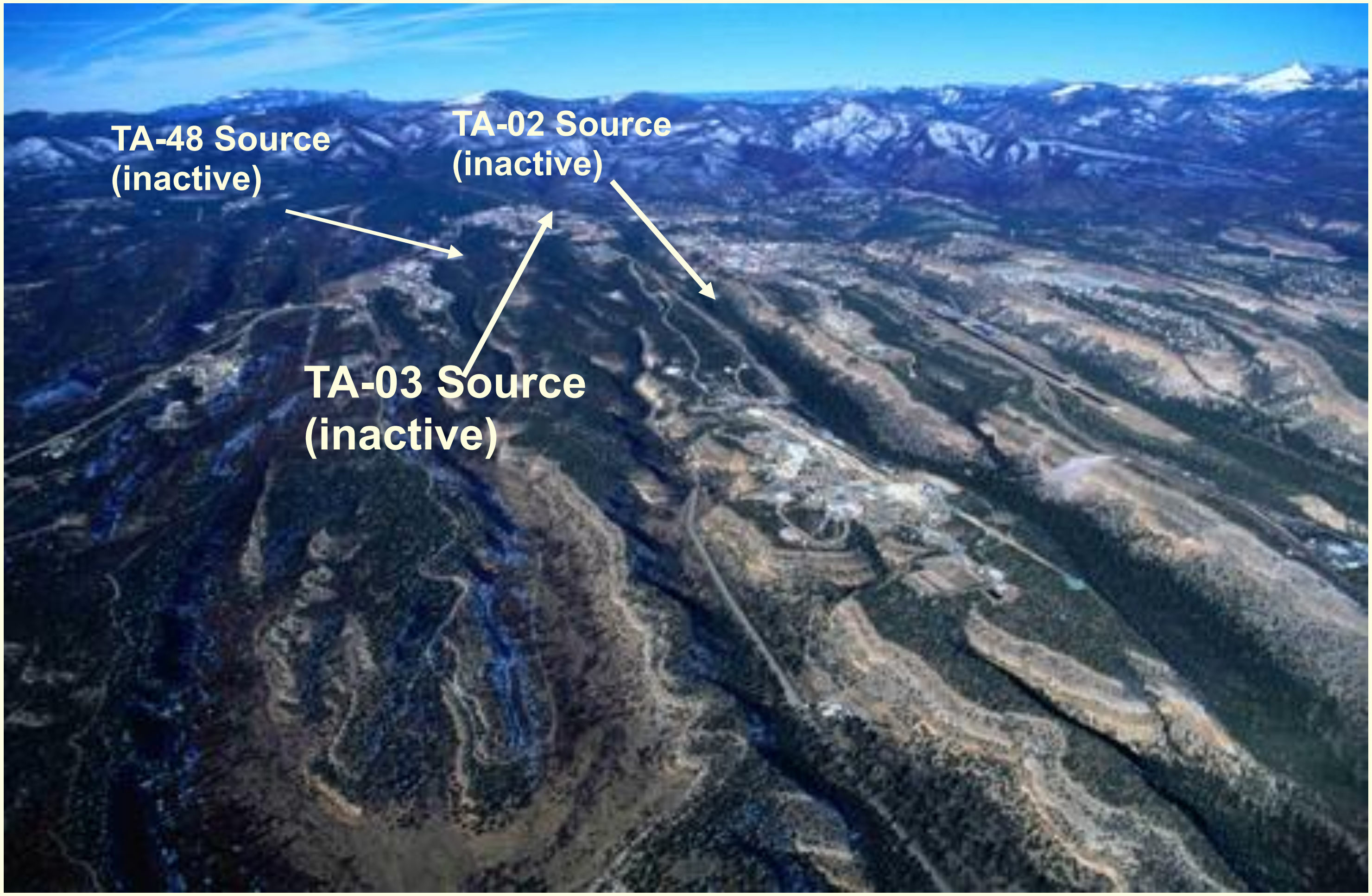
V. Fate and Transport of Chromium

VI. Natural Attenuation

VII. Remediation Options

VIII. Summary and Conclusions

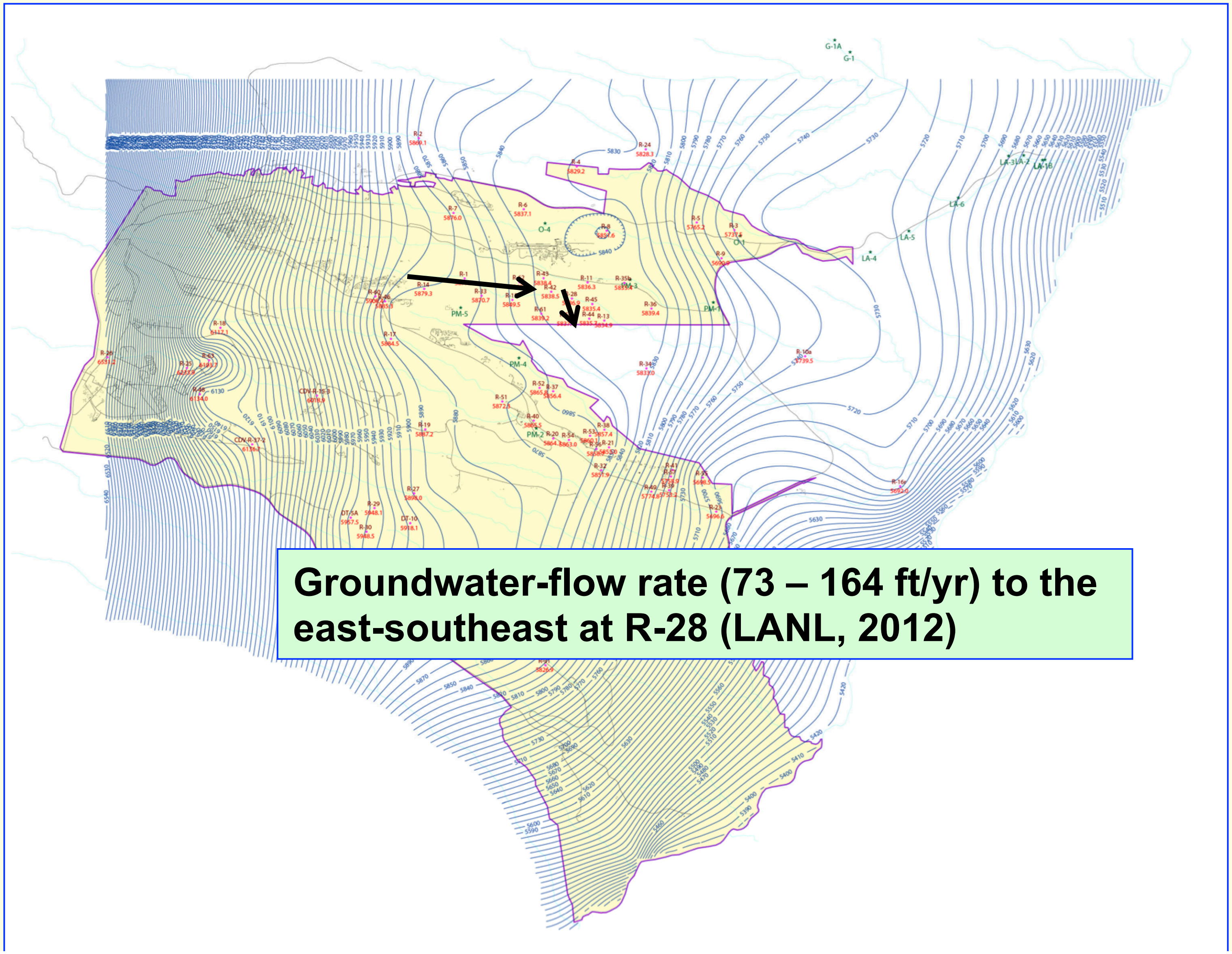
Photograph of the Jemez Mountains and Pajarito Plateau
(view to the west with industrial sources of chromium(VI) discharges)



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

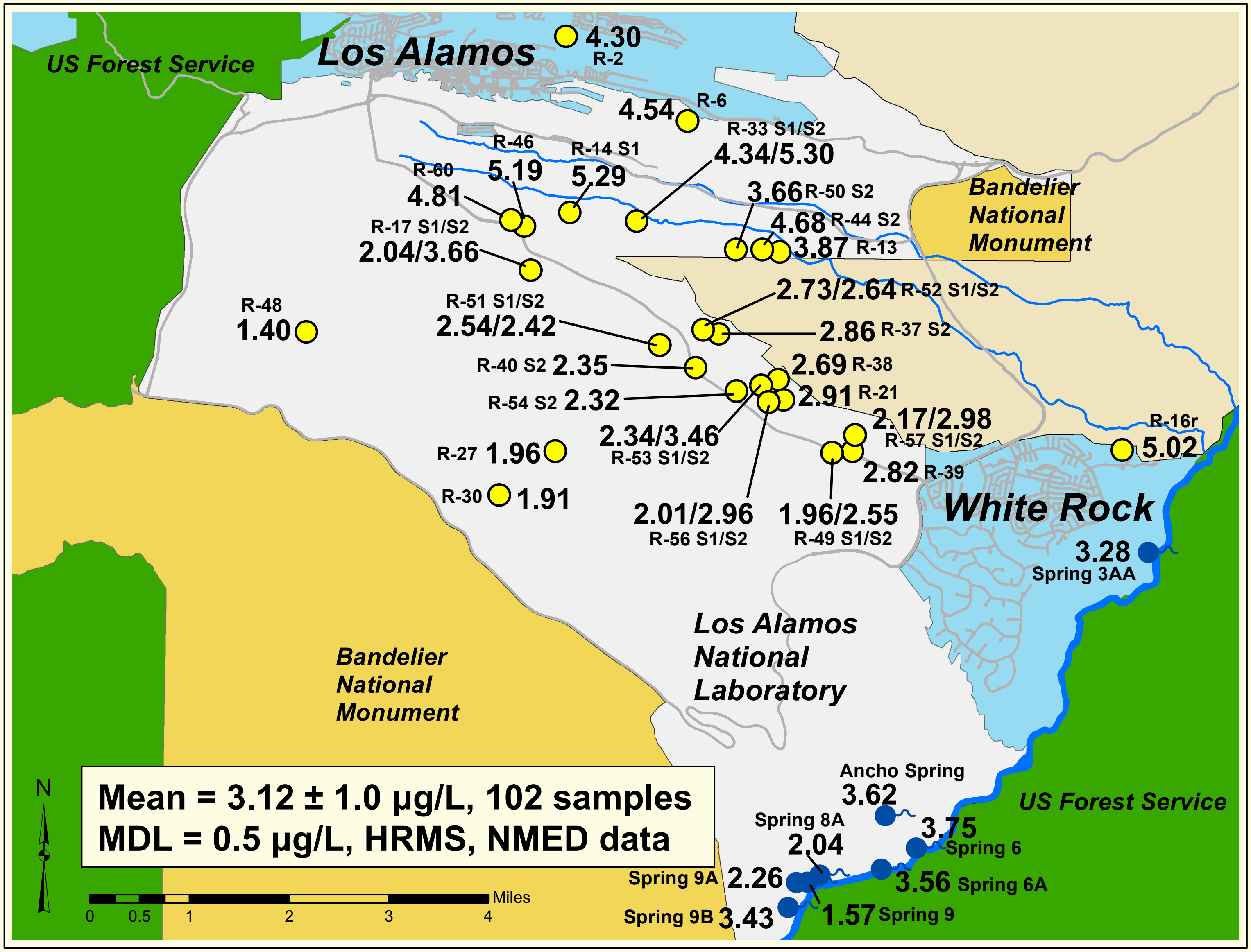
- **Over 15 years of Cr(VI) releases from the TA-03 cooling tower**
- **Between 31,000 and 72,000 kg of Cr(VI), with a mean of 54,000 kg, were released between 1956 and 1972 into Sandia Canyon**
- **Most of the Cr(VI) released is from dissociation of potassium dichromate ($K_2Cr_2O_7$)**
- **Approximately 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**

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



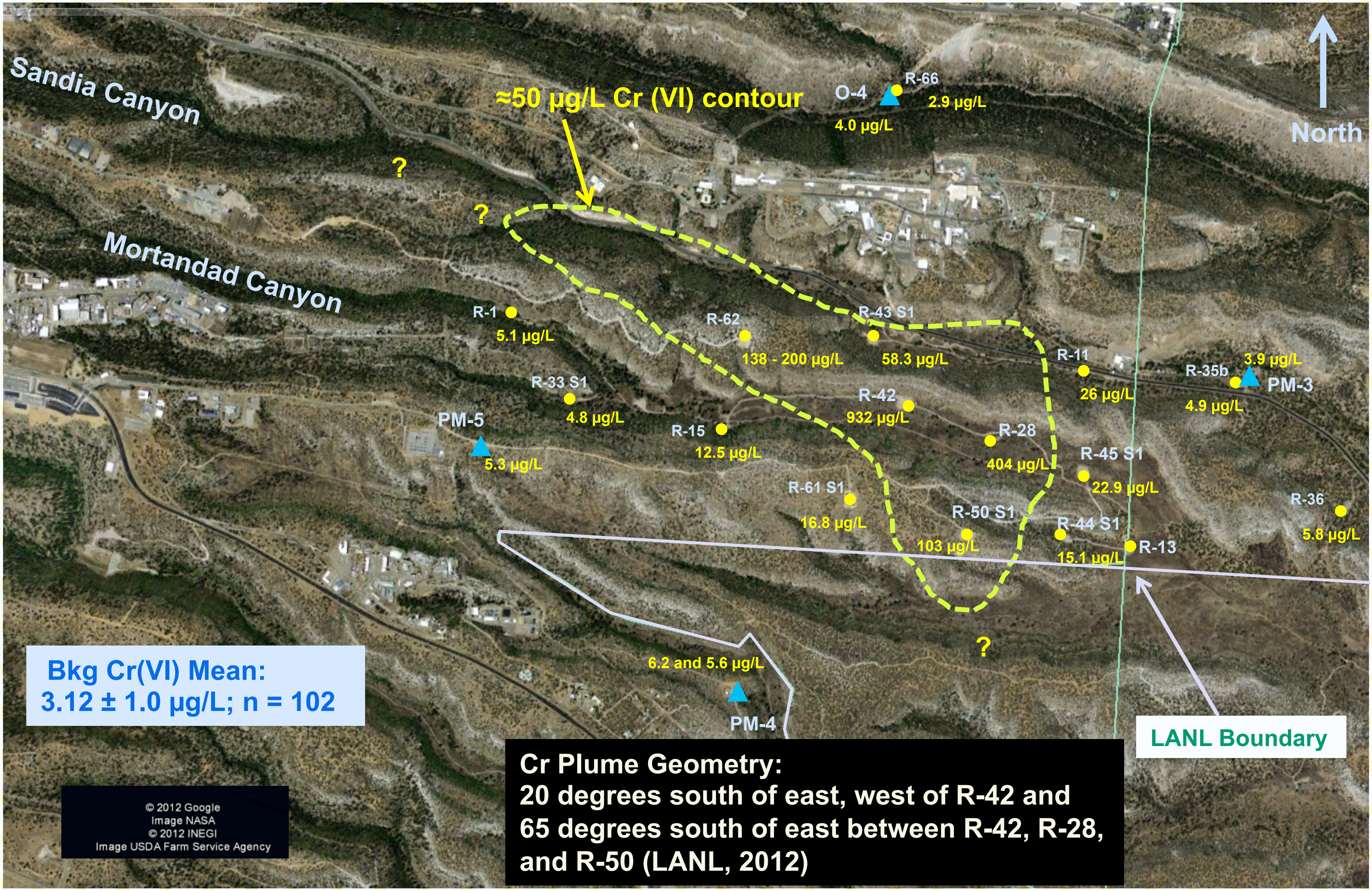
Groundwater-flow rate (73 – 164 ft/yr) to the east-southeast at R-28 (LANL, 2012)

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, HRMS, NMED data

Concentrations of Cr in the Regional Aquifer, LANL, NM



▲ 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.

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

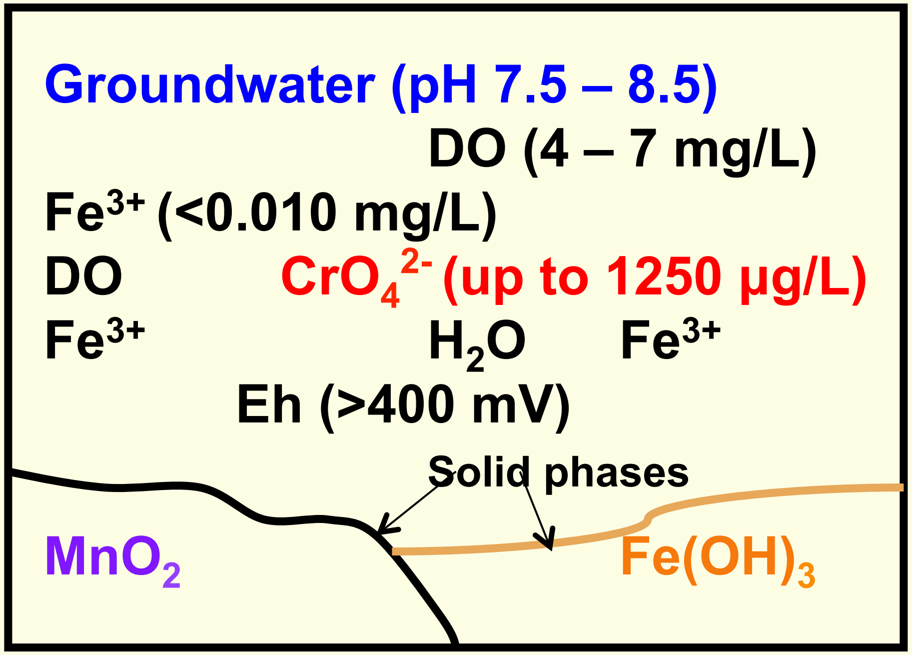
(131 feet/year)/1.5 = 83 feet/year; and

(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.

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

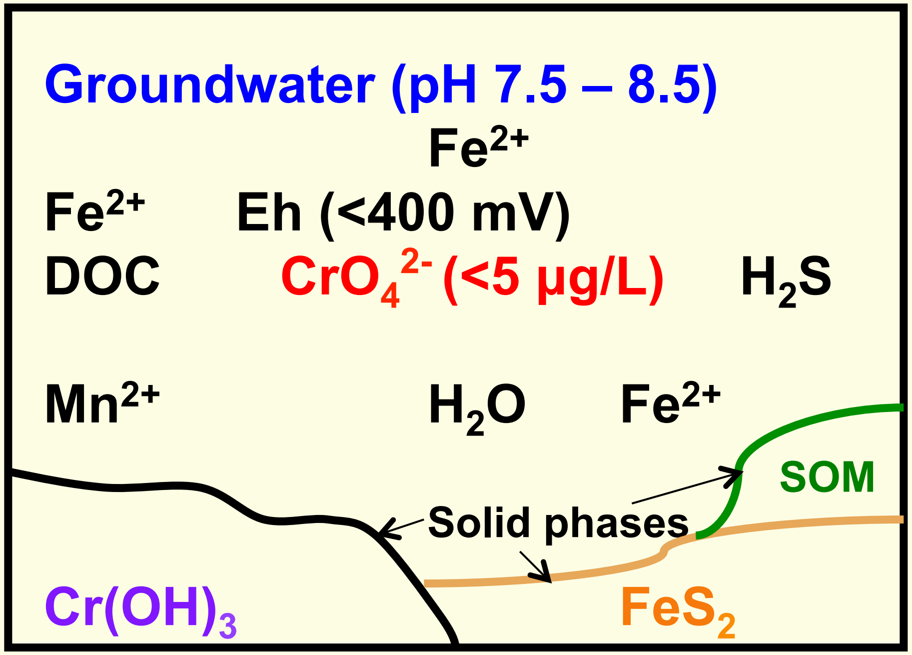


Aquifer System Characteristics

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

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

Chromium Removal in Aquifer Systems Containing Reductive Minerals and Reducing Groundwater

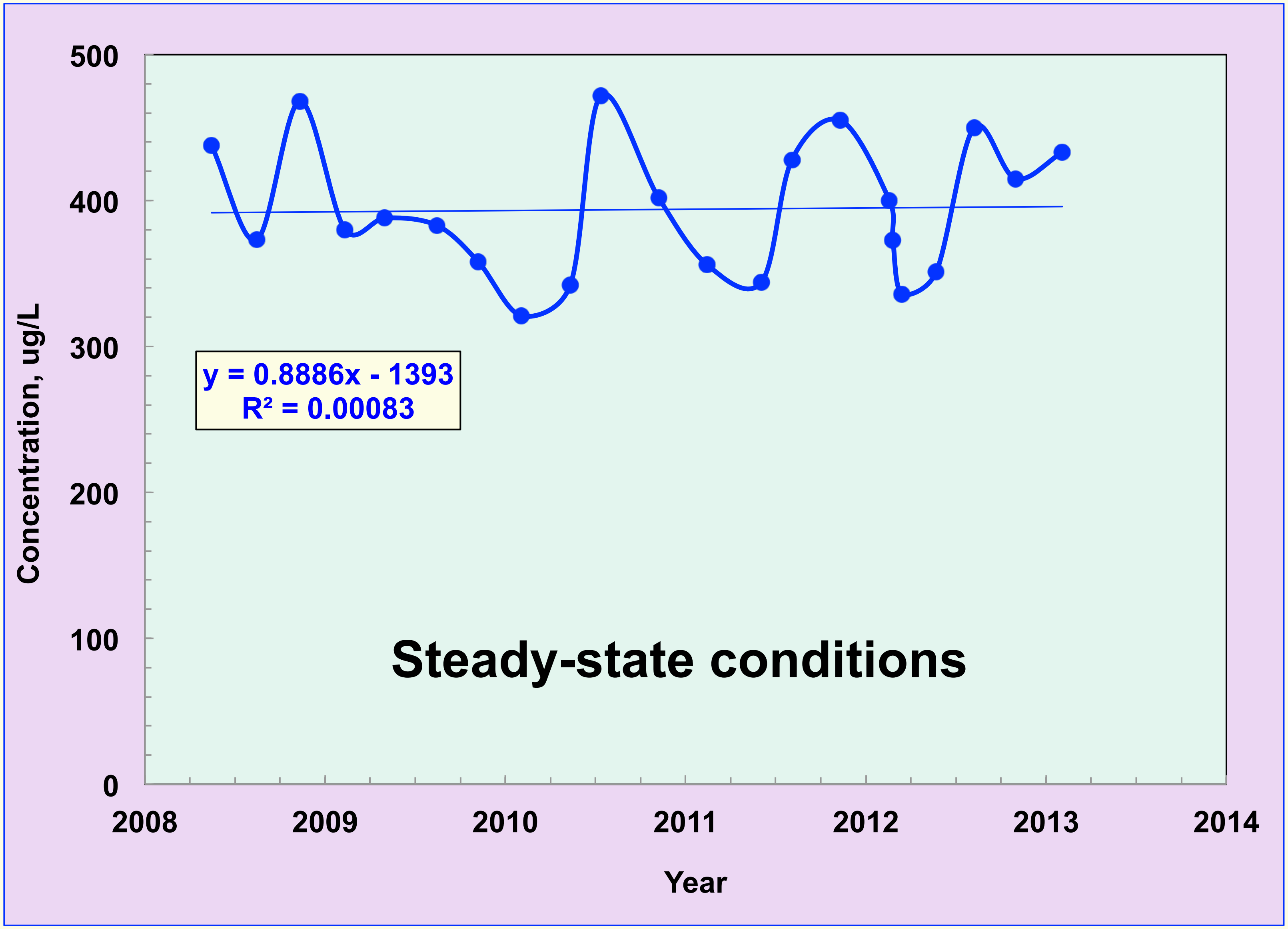


Aquifer System Characteristics

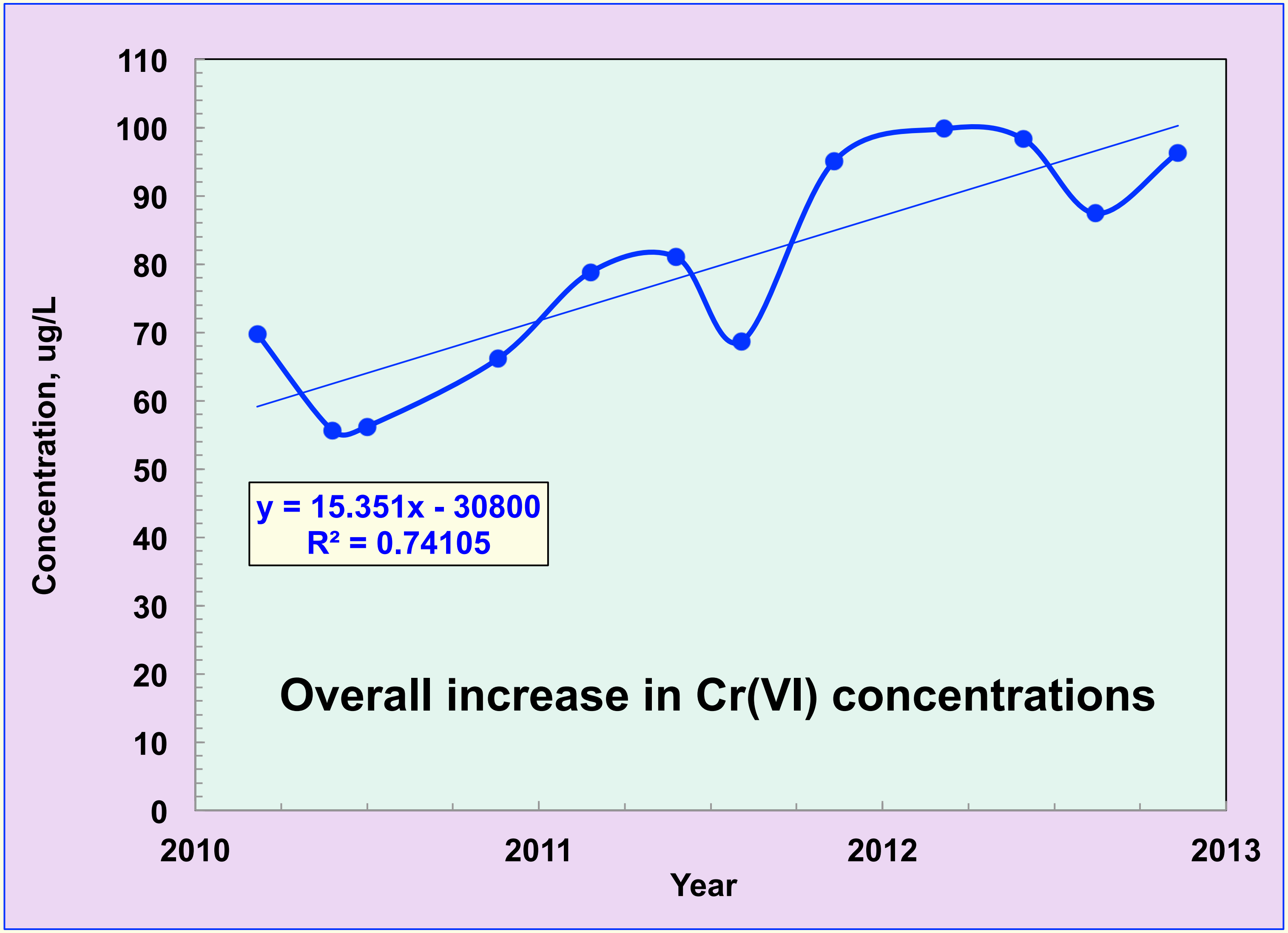
Reduced iron (Fe^{2+})	Dissolved sulfide (H_2S)
Reduced iron [FeS_2]	Dissolved organic carbon (DOC)
Reduced manganese (Mn^{2+})	Solid Organic Matter (SOM)
Reduced chromium [$Cr(OH)_3$]	
Oxidized chromium [CrO_4^{2-}] (chromate)	

Reduction-Oxidation with Iron (Fe) and Chromium (Cr)

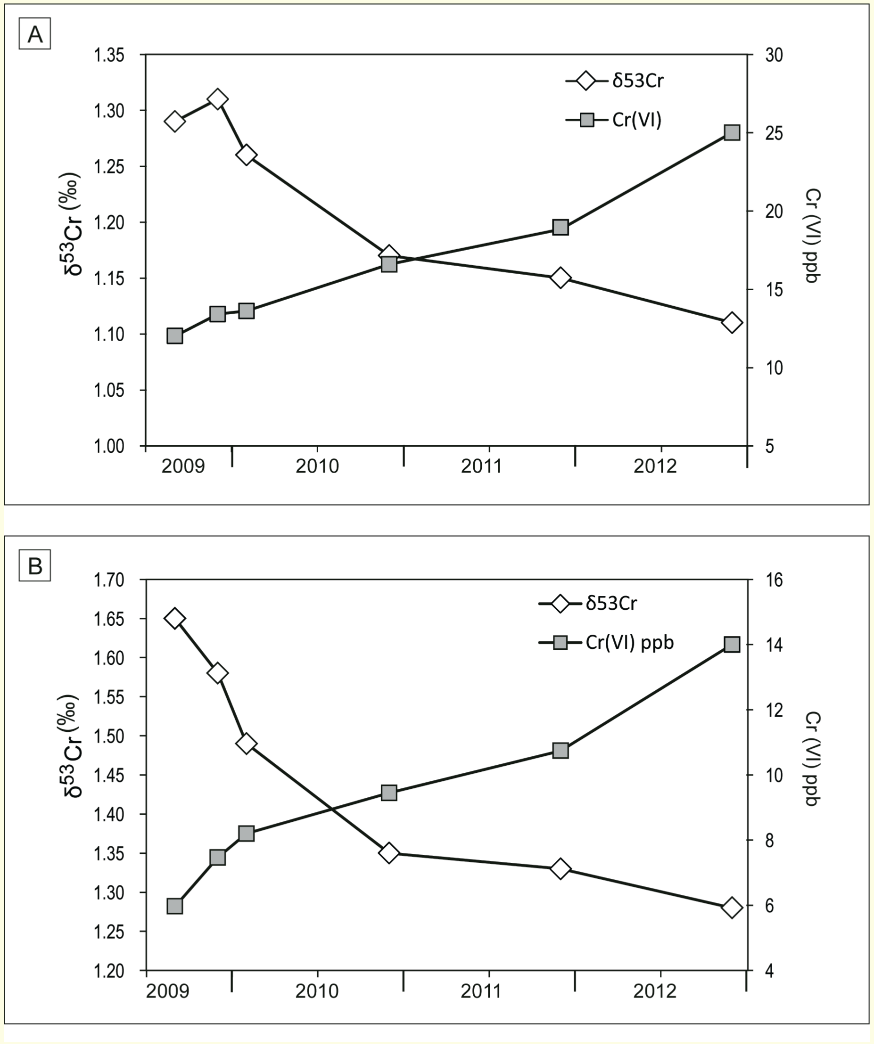
Dissolved Concentrations of Chromium at Regional Aquifer Well R-28, Los Alamos, New Mexico



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

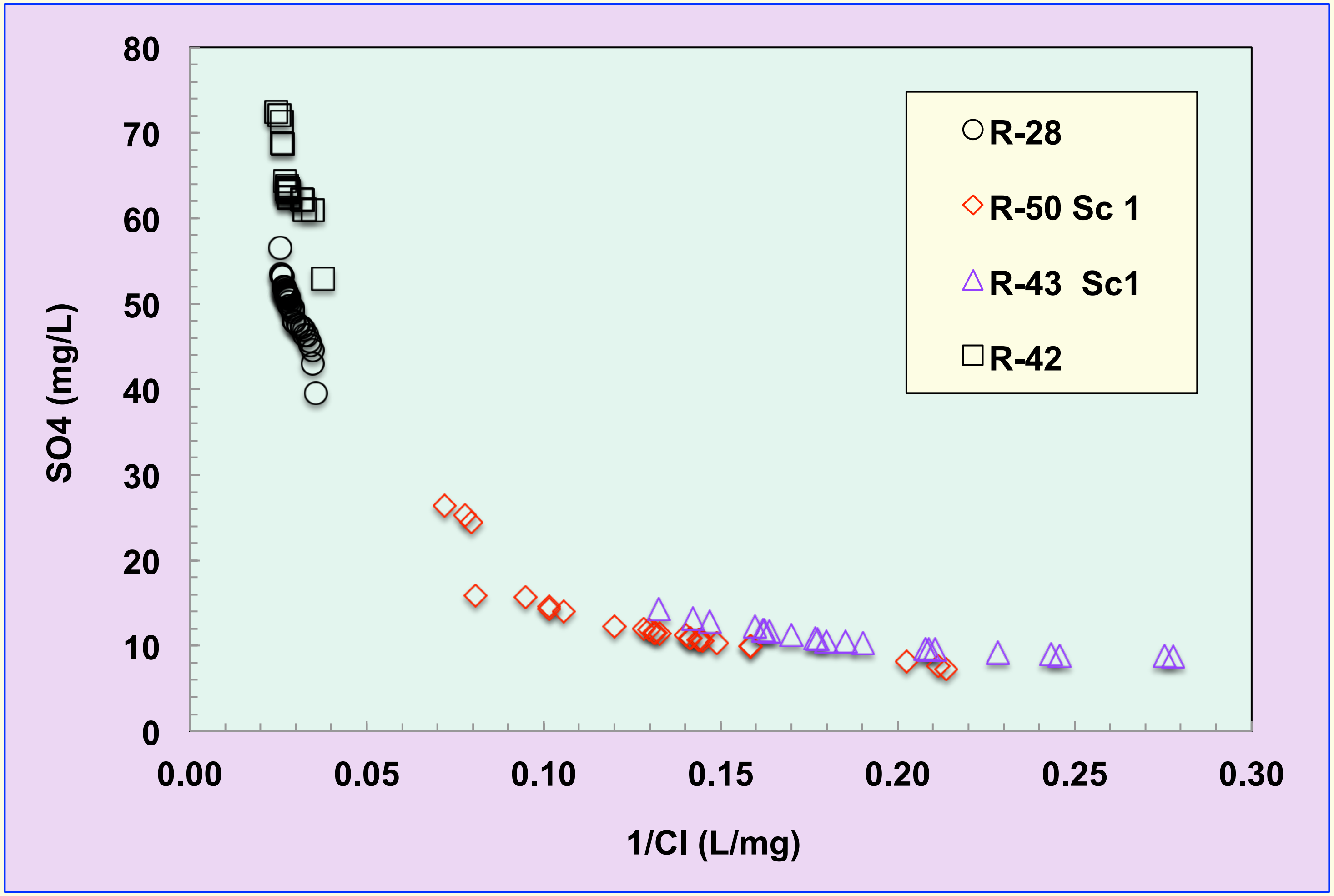


Concentrations of Chromium(VI) Versus δ^{53}Cr Ratios at Regional Aquifer Well R-45 Screens 1(A) and 2(B), Los Alamos, New Mexico

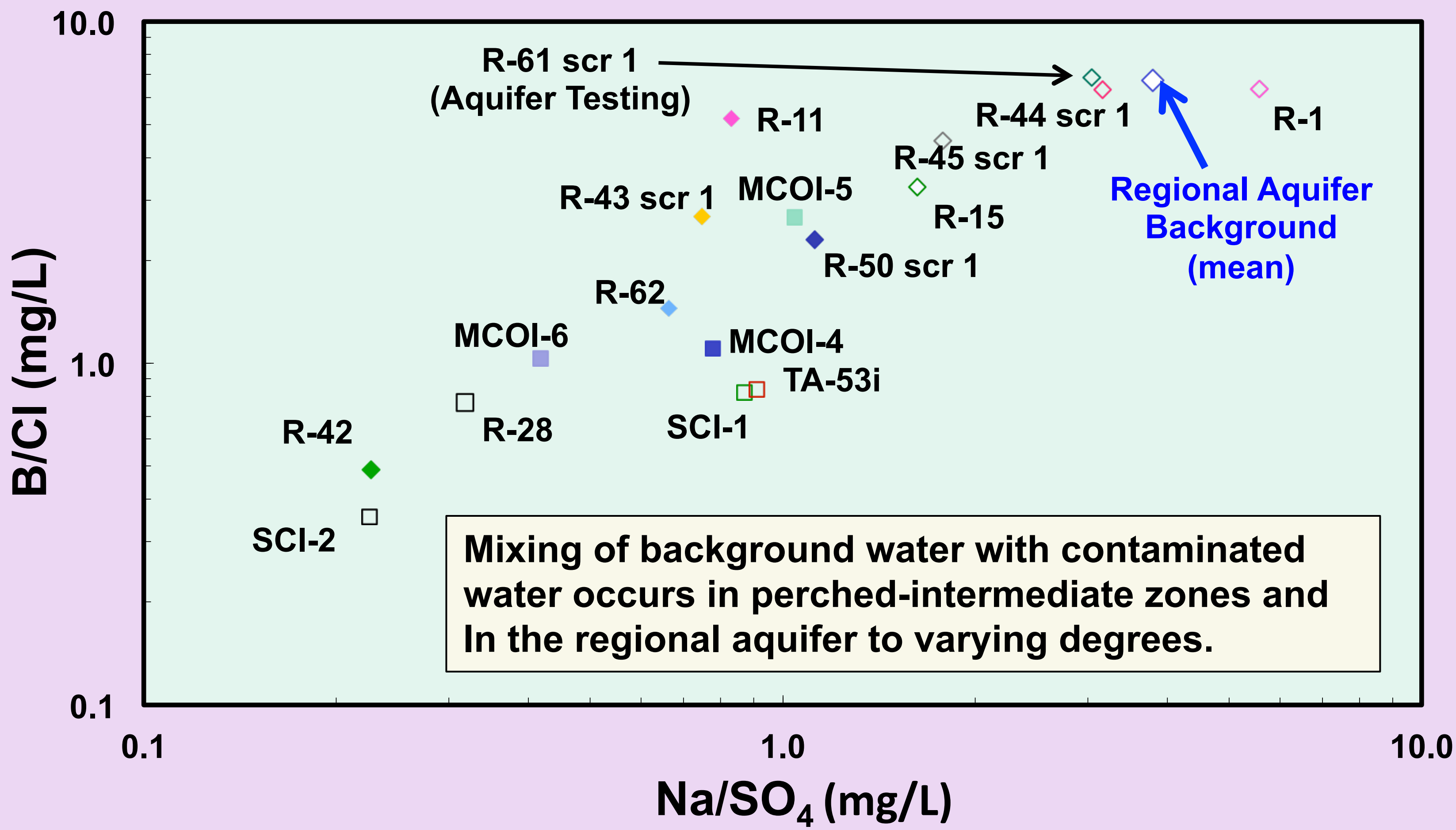


Los Alamos National Laboratory(LANL), 2012, Phase II Investigation Report for Sandia Canyon, LA-UR-1224593, EP2012-0195, various pagination.

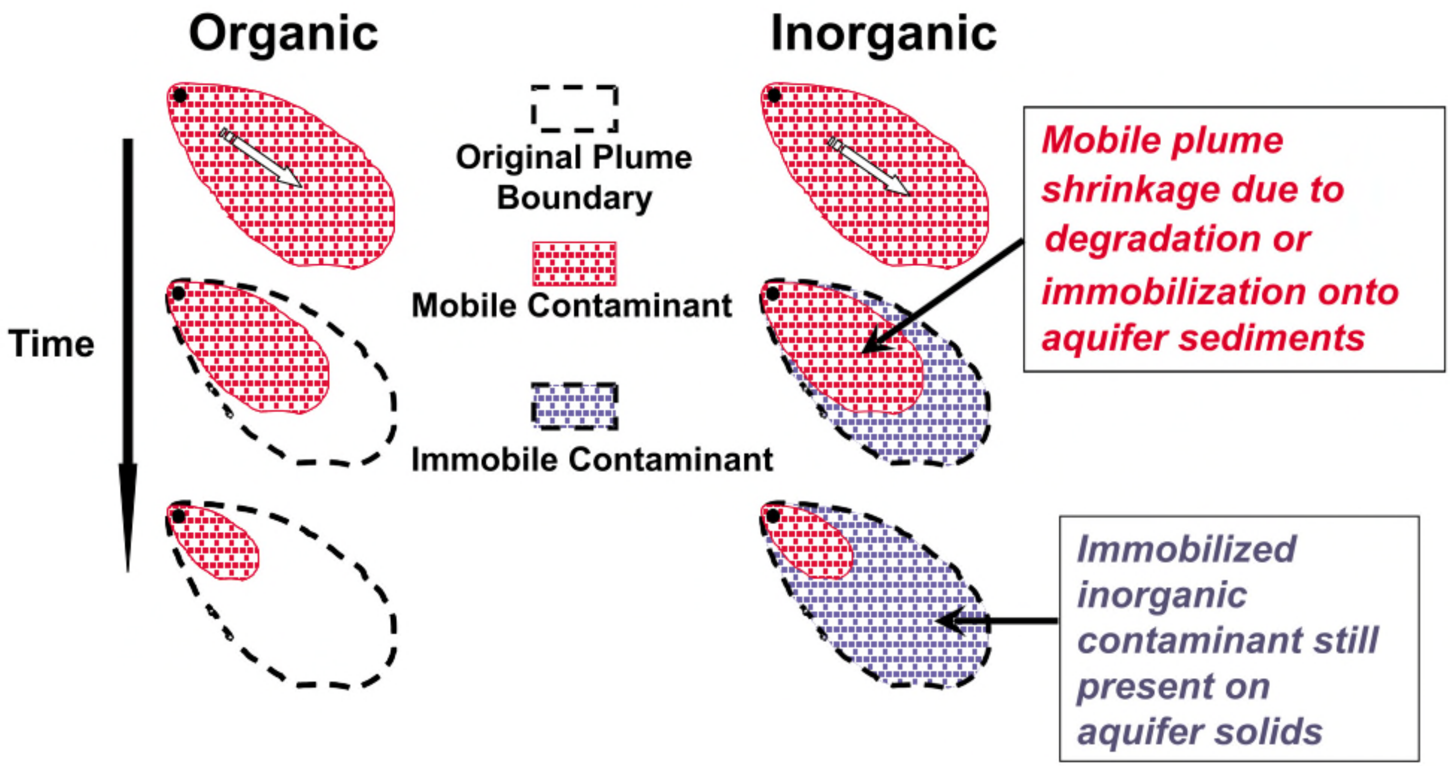
Dissolved Concentrations of 1/Chloride Versus Sulfate in the Regional Aquifer, Los Alamos, NM



Sodium/Sulfate Versus Boron/Chloride in Groundwater, Los Alamos National Laboratory, New Mexico



Conceptual Diagrams of Monitored Natural Attenuation for Organic and Inorganic Plumes in Groundwater (EPA, 2007)



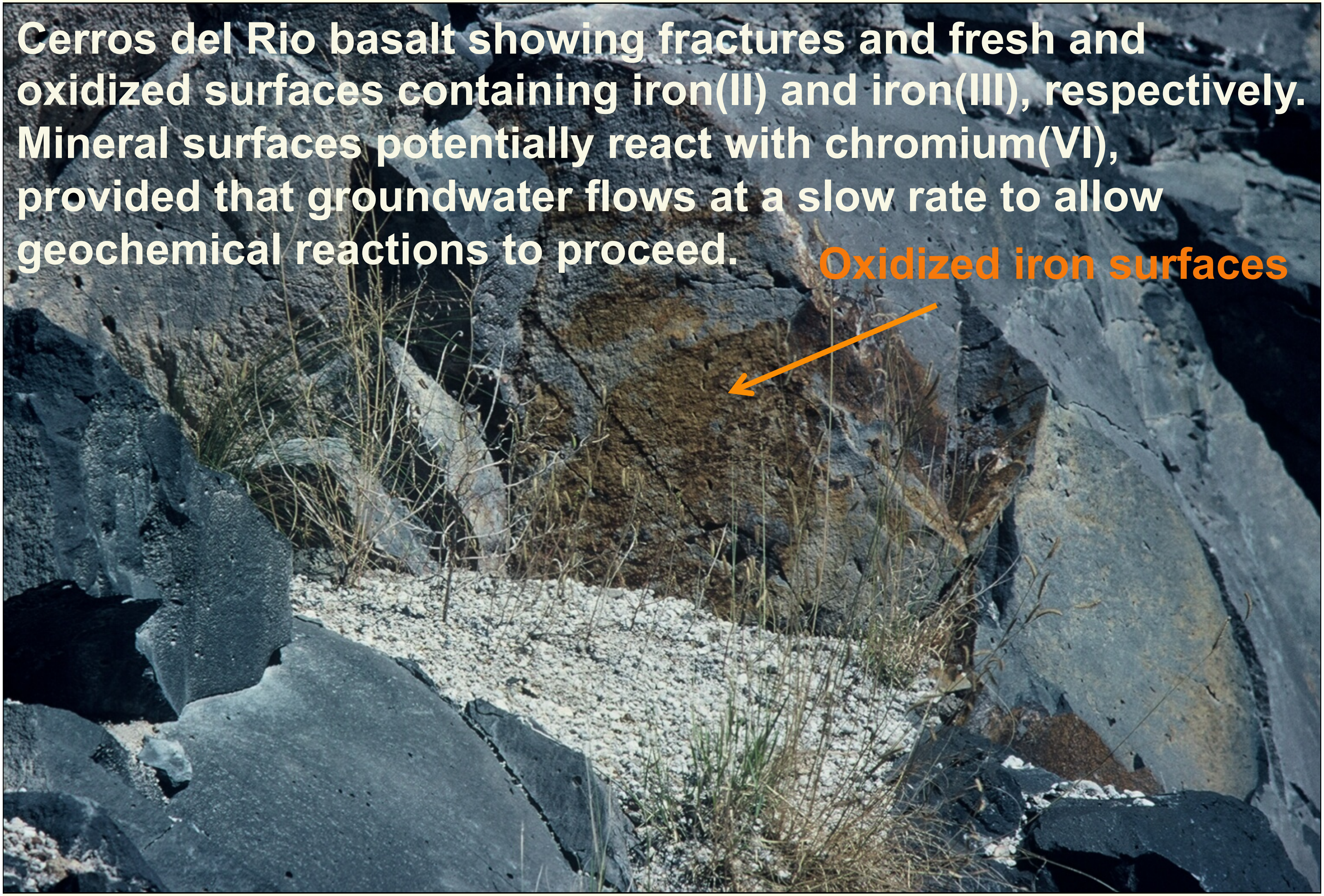
Conceptual distinction between organic versus inorganic contaminant plume behavior where natural processes are active within the ground-water aquifer. Natural attenuation of inorganic contaminants is viable only if the immobilized contaminant remains stable and resistant to remobilization during changes in ground-water chemistry.

Criteria for Natural Attenuation of Chromium (EPA)

- **Natural attenuation of chromium in aquifer systems is supported by:**
- **Decreasing concentrations of chromium(VI) over time;**
- **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.



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.

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

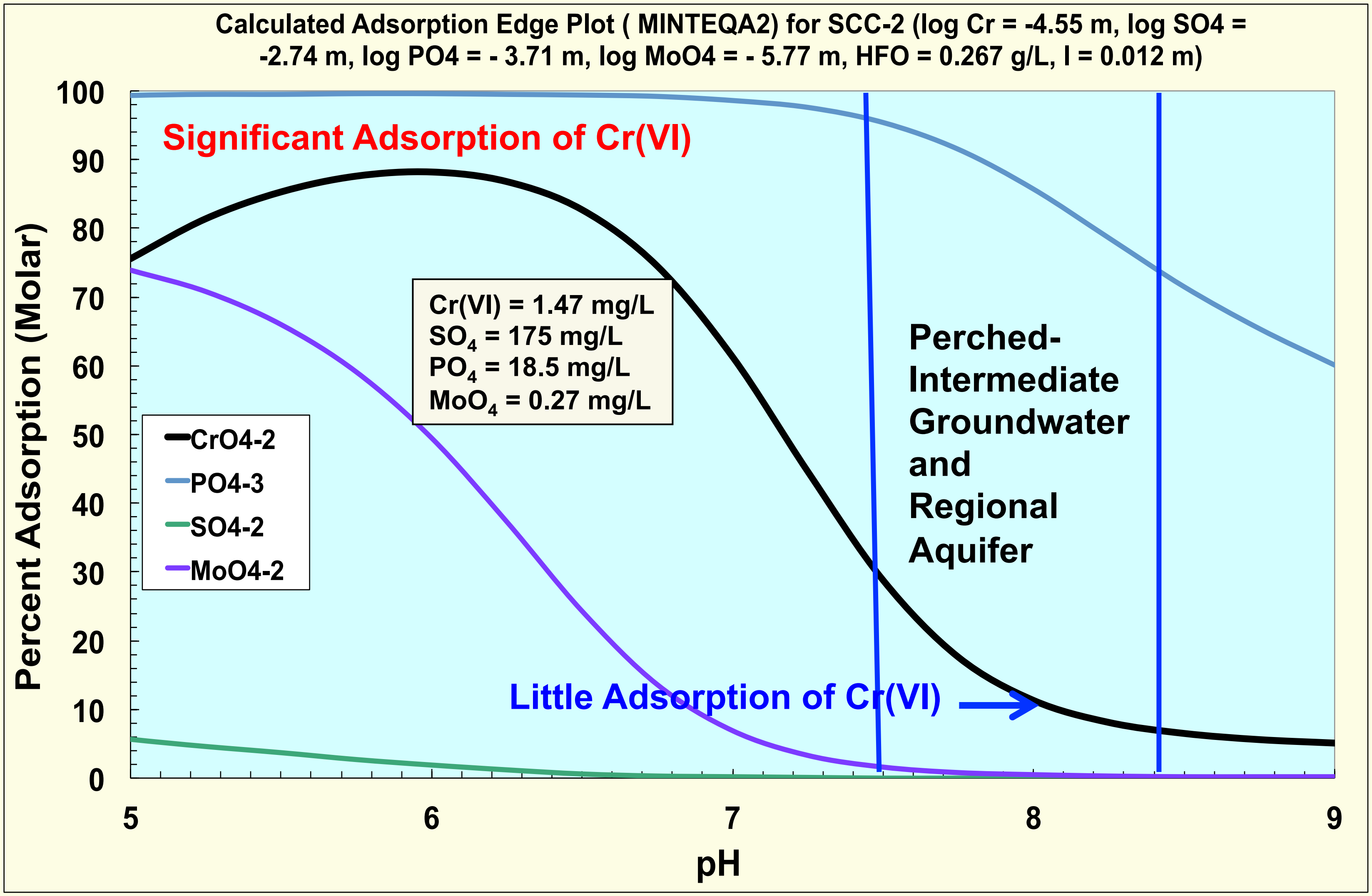
- Soluble chromium(VI) is stable in the regional-aquifer system characterized by strongly oxidizing conditions with respect to iron, dissolved oxygen, and manganese.
- Chromium is migrating at nearly the same rate of groundwater flow within the regional aquifer (Puye Formation and Miocene pumiceous sediments).
- 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

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



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