

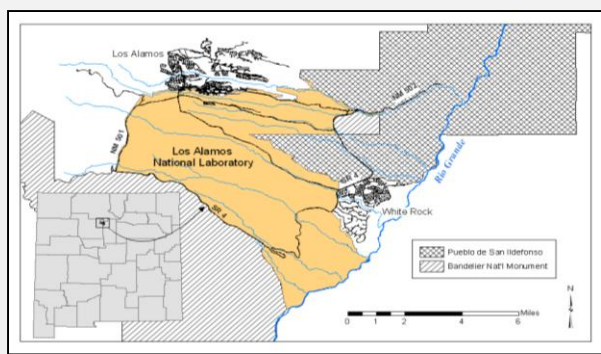


Aqueous Chemistry of Chromium in an Oxidizing Aquifer System, Pajarito Plateau, New Mexico

GRANZOW, Kim¹, DALE, Michael², LONGMIRE, Patrick¹, YANICAK, Stephen¹, and KULIS, Jerzy², (1)New Mexico Environment Department, DOE Oversight Bureau, 1183 Diamond Drive, Suite B, Los Alamos, NM 87544 (2)New Mexico Environment Department, 2905 Rodeo Park Drive East, Bldg 1, Santa Fe, NM 87505-6303

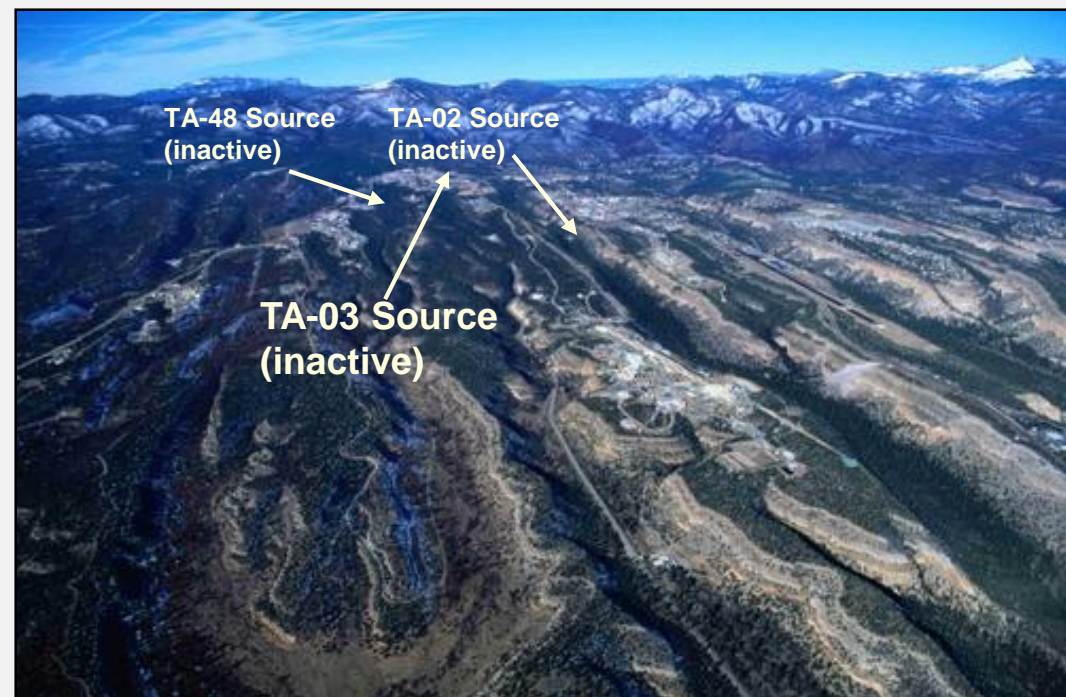
Abstract

Chromium (Cr) is a trace element of considerable interest to aqueous geochemists, environmental scientists, and toxicologists due to high toxicity of Cr(VI). Chromium(VI) is stable under oxidizing conditions, forming soluble dichromate, bichromate, and chromate. Chromium(III) hydroxide precipitates under relatively reducing conditions, and equilibrium concentrations of Cr are typically less than 9.62e-05 mM (0.005 mg/L) under circumneutral pH conditions. Potassium dichromate (31,000 to 72,000 kg) was used as an anticorrosion agent at a cooling tower at Los Alamos National Laboratory (LANL) from 1956 to 1972 and was discharged to a watershed. Chromate has migrated approximately 290 meters through the vadose zone under fracture and porous media flow conditions to reach the regional water table. The transport time for Cr(VI) migrating through the vadose zone downgradient from the main discharge source is estimated at less than 26 years. Background concentrations of total dissolved Cr in the regional aquifer, mainly in the form of Cr(VI), range from 5.77e-05 to 9.62e-05 mM (0.003 to 0.005 mg/L), while concentrations of anthropogenic chromate reach 0.024 mM (1.248 mg/L). First-order calculations suggest that Cr(VI) migration within the regional aquifer at LANL is approximately equal to the average advective groundwater-flow rates ranging from 21 to 50 m/yr. Total dissolved concentrations of Cr show either steady-state or increasing trends at monitoring wells over time, suggesting that natural attenuation of Cr is not occurring to a significant extent. The Cr trends suggest that there are multiple entry points to the regional-water table from more than one source. The regional aquifer is characterized by a calcium-sodium-bicarbonate composition and is oxidizing with respect to Fe and Mn. This aquifer contains measurable concentrations of dissolved oxygen ranging from 0.16 to 0.25 mM (5.12 to 8.0 mg/L). Adsorption of Cr(VI) onto regional aquifer sediments is limited by adsorbents with small surface areas (hematite and silicates), presence of competing oxyanions (sulfate and bicarbonate), and basic pH conditions. Reduction of Cr(VI) to Cr(III) is limited by the scarcity of electron donors, including reactive Fe(II) phases, dissolved and solid organic carbon, and dissolved sulfide.



Regional setting of Los Alamos National Laboratory

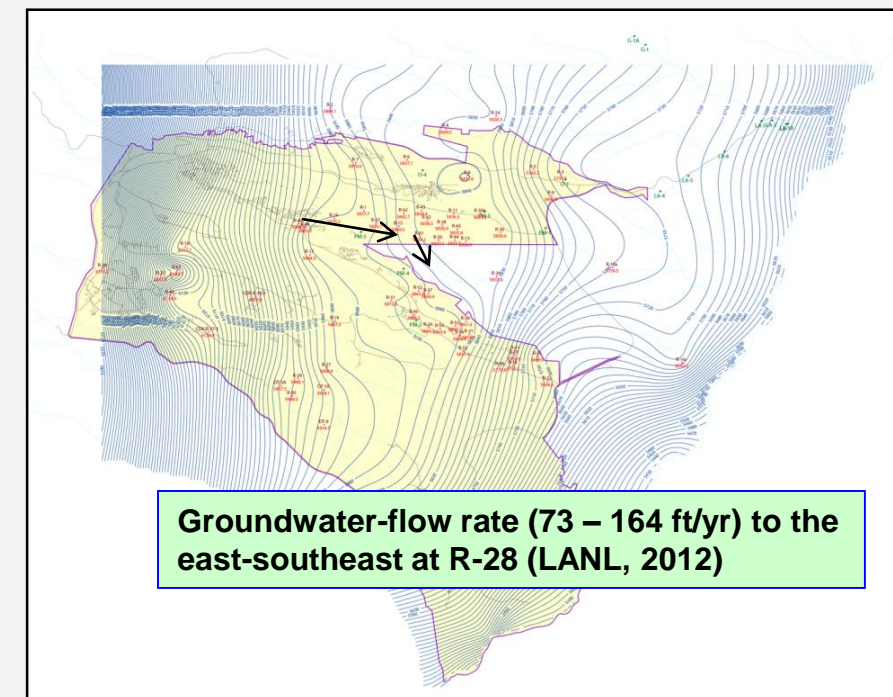
Photograph of the Jemez Mountains and Pajarito Plateau (view to the west with industrial sources of chromium(VI) discharges)



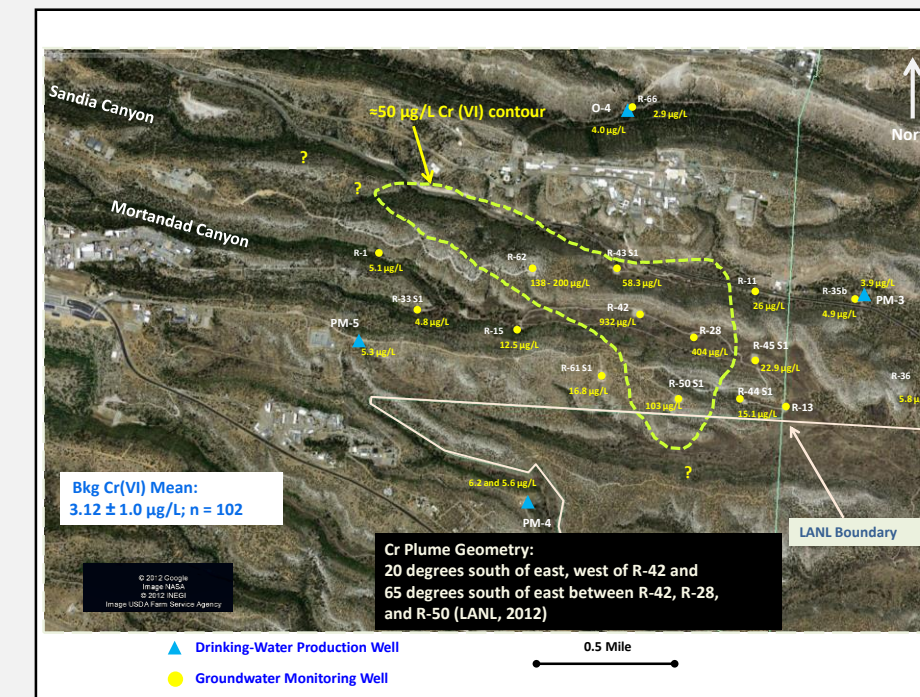
Chromium Releases at Technical Area-03, Los Alamos National Laboratory

- 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)



Concentrations of Chromium in the Regional Aquifer, Los Alamos National Laboratory, New Mexico



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;

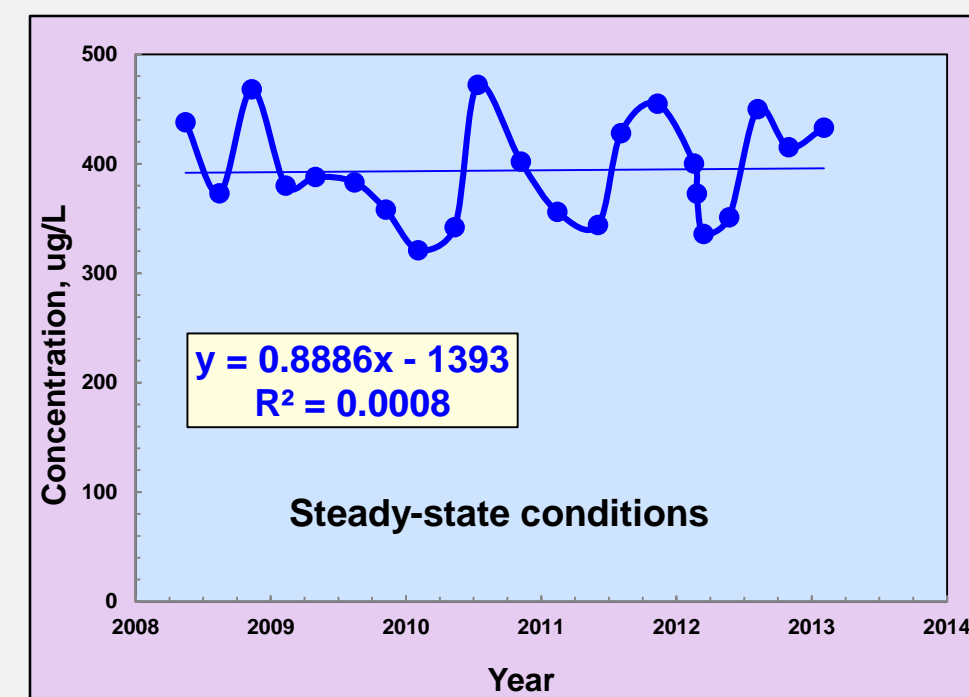
(131 feet/year)/1.5 = 83 feet/year; and

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

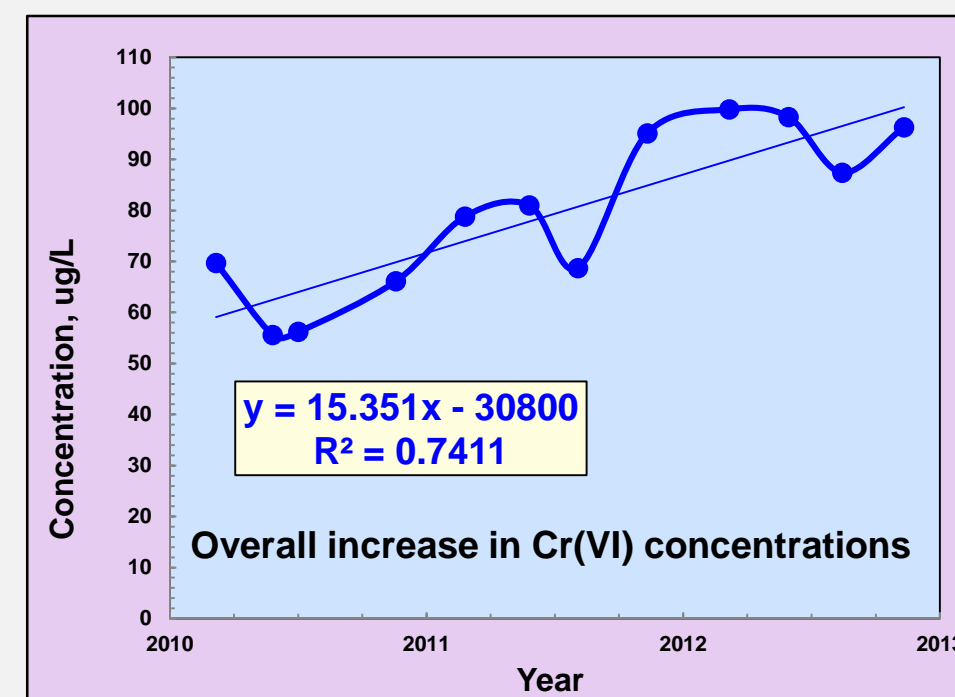
The most representative Cr transport rates most likely range from 83 to 109 feet/year in the regional aquifer at R-28. This range is based on extensive monitoring data provided by LANL (2012) and NMED and Cr trend analysis.

R_f is the retardation factor ($1 + pK_d/n_e$), where p (1.5g/cm³), K_d (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.

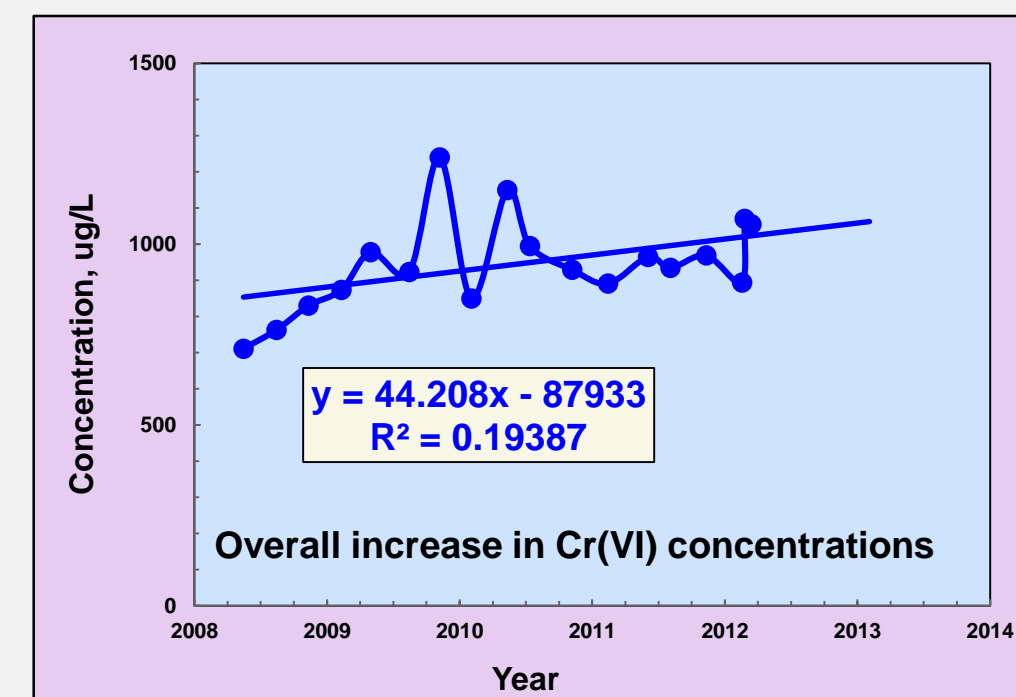
Dissolved Concentrations of Chromium at Regional Aquifer Well R-28, Los Alamos, New Mexico



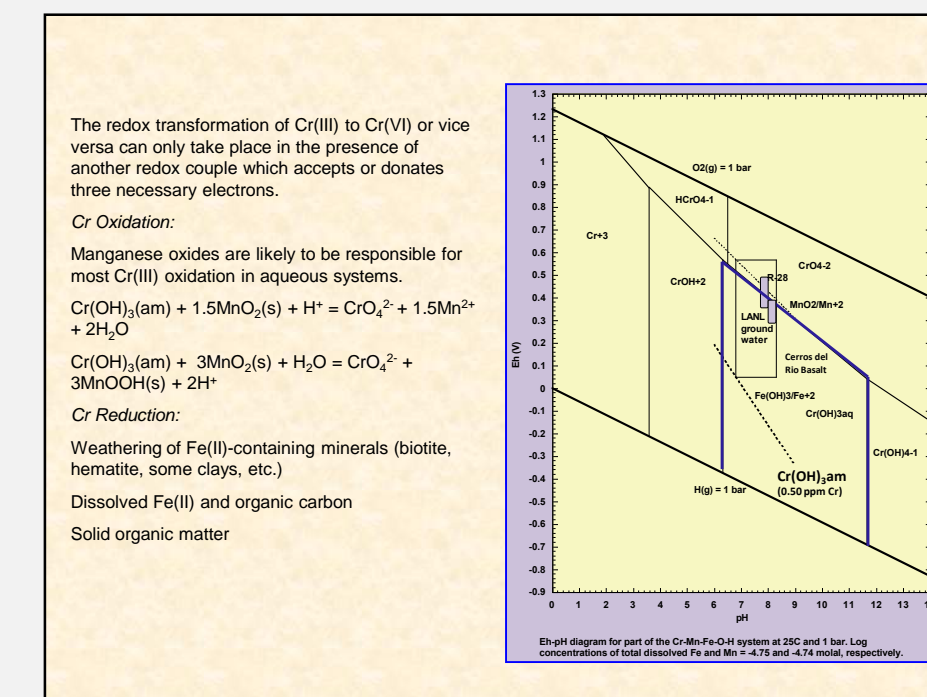
Dissolved Concentrations of Chromium at Regional Aquifer Well R-50 Screen 1, Los Alamos, New Mexico



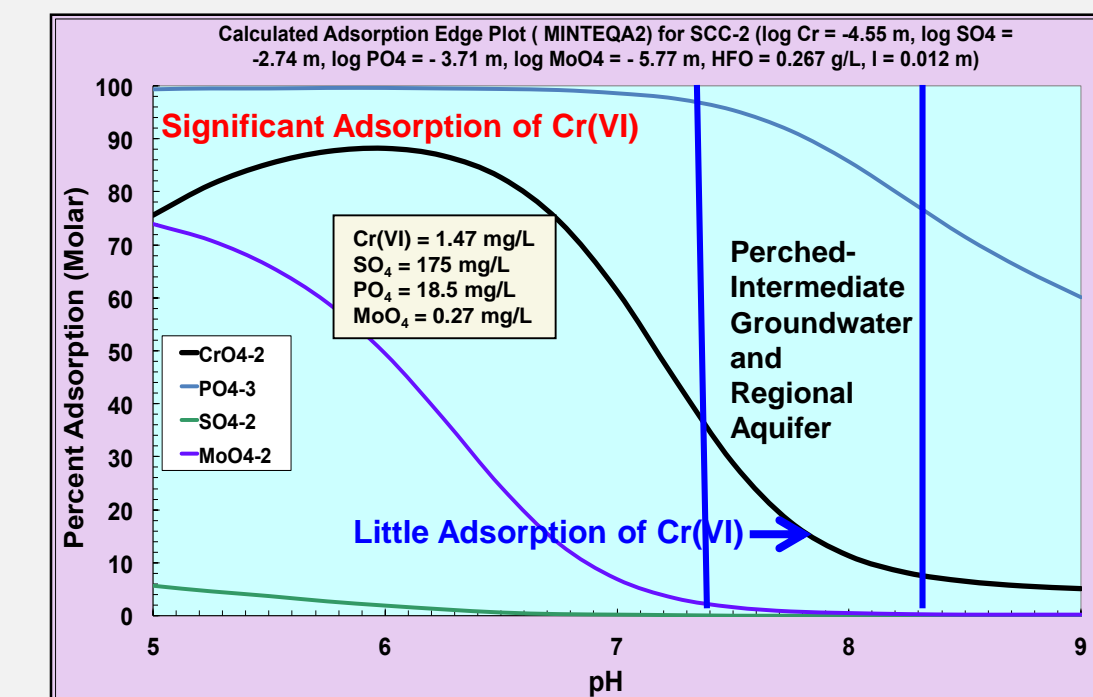
Dissolved Concentrations of Chromium at Regional Aquifer Well R-42, Los Alamos, New Mexico



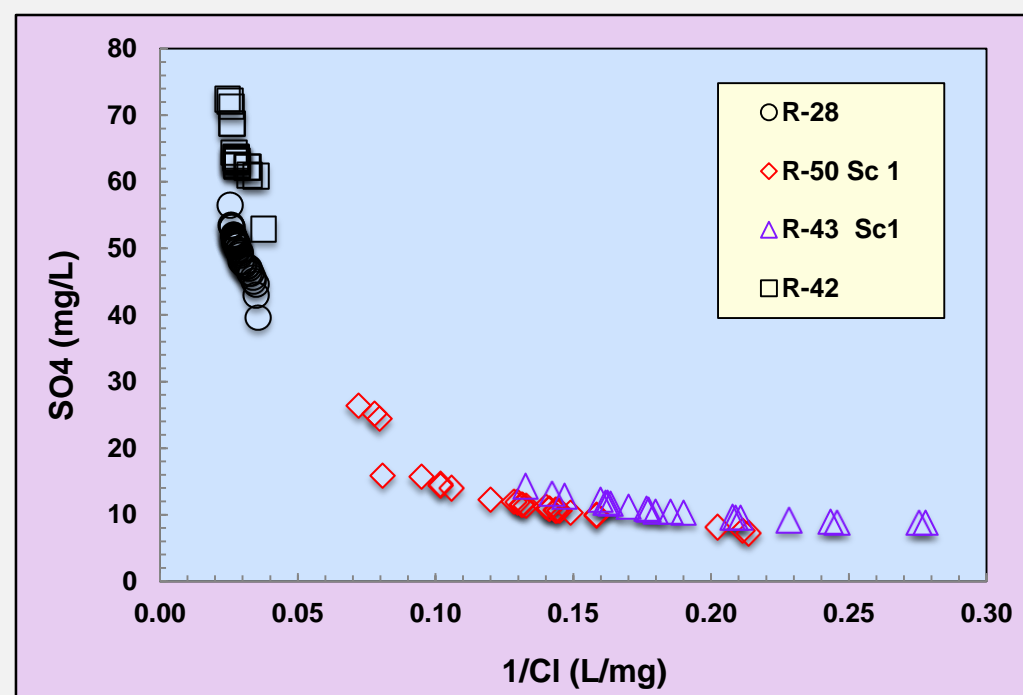
Redox Behavior of Chromium in Aqueous Environments



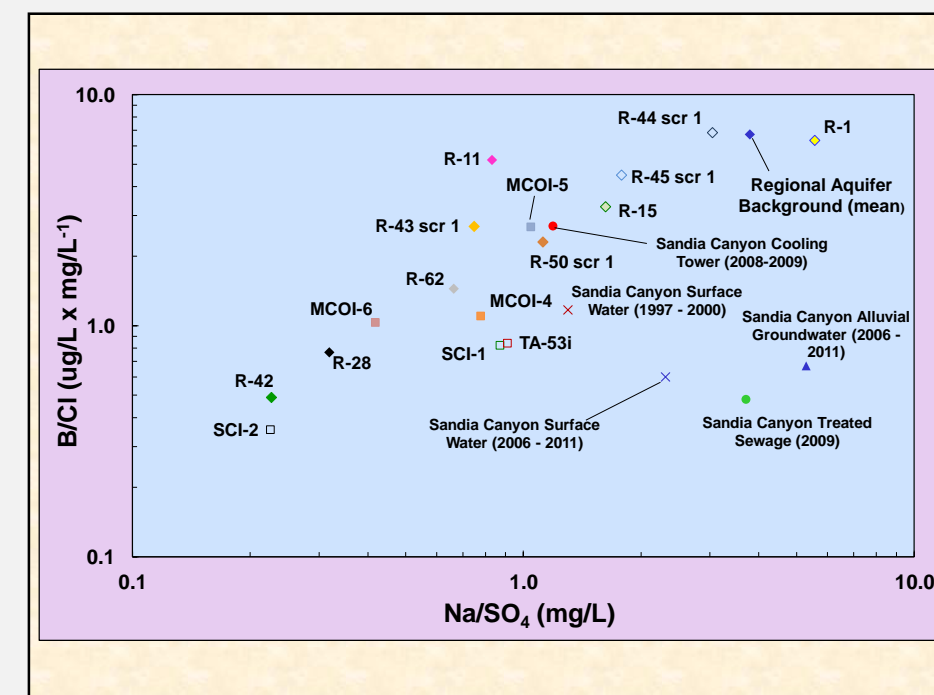
Calculated Adsorption Edge Plot Using MINTEQA2 for the Unsaturated Zone, Sandia Canyon, New Mexico



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



Evaluation of Natural Attenuation of 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 (New Mexico groundwater standard) 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:
 - 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_2 , 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_2), 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.

For additional information please contact Kim Granzow at kgranzow@lanl.gov or (505) 661-4008

DATA SOURCES: (1) New Mexico Environment Department
(2) LANL Earth and Environmental Sciences Geology and Geochemistry Research Lab (EES-14 GGRL)
(3) Intellus New Mexico Database: <http://www.intellusnmdata.com/>

Acknowledgment: "This material is based upon work supported by the Department of Energy Office of Environmental Management under Award Number(s) DE-EM0002420."Disclaimer: "This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."