CHROMIUM GEOCHEMISTRY IN A WETLAND ENVIRONMENT

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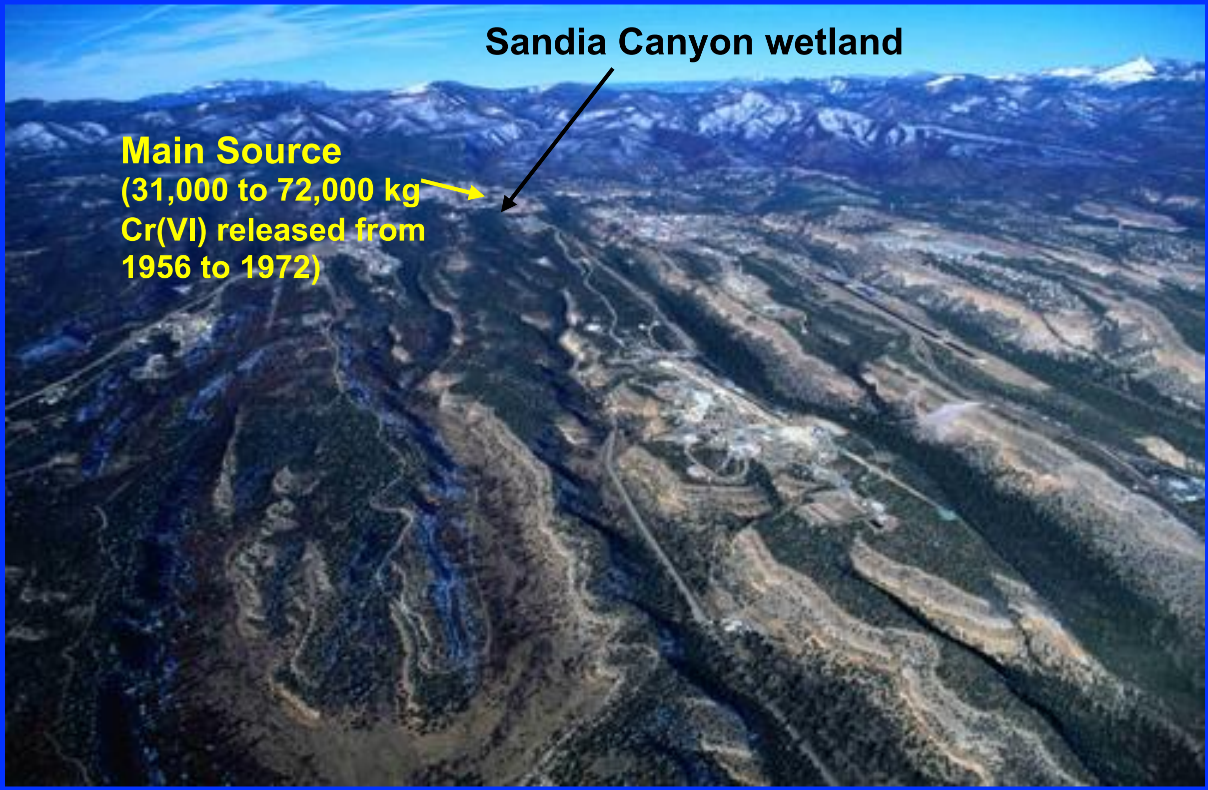
Purpose and Scope

Evaluate geochemical processes (redox, adsorption, and precipitation) controlling the stability of chromium within the Sandia Canyon wetland, Los Alamos, New Mexico.

Topics of interest for chromium include:

- **Sources and Mass Balance**
- **Speciation**
- **Current Conditions in Sandia Wetland**
- **Results of Wetland Drying Experiments**

Photograph of the Jemez Mountains and Pajarito Plateau
(view to the west with past industrial source of $K_2Cr_2O_7$ discharges)



Analytical Methods for Chromium

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (EPA Method 200.8) for total Cr

Method detection limit is 1.9E-08 M (1 μg/L), depending on sample dilution.

Ion Chromatography (IC) (EPA Method 218.6) for Cr(VI)

Method detection limit is 9.6E-10 M (0.05 μg/L), depending on sample matrix.

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.

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.

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

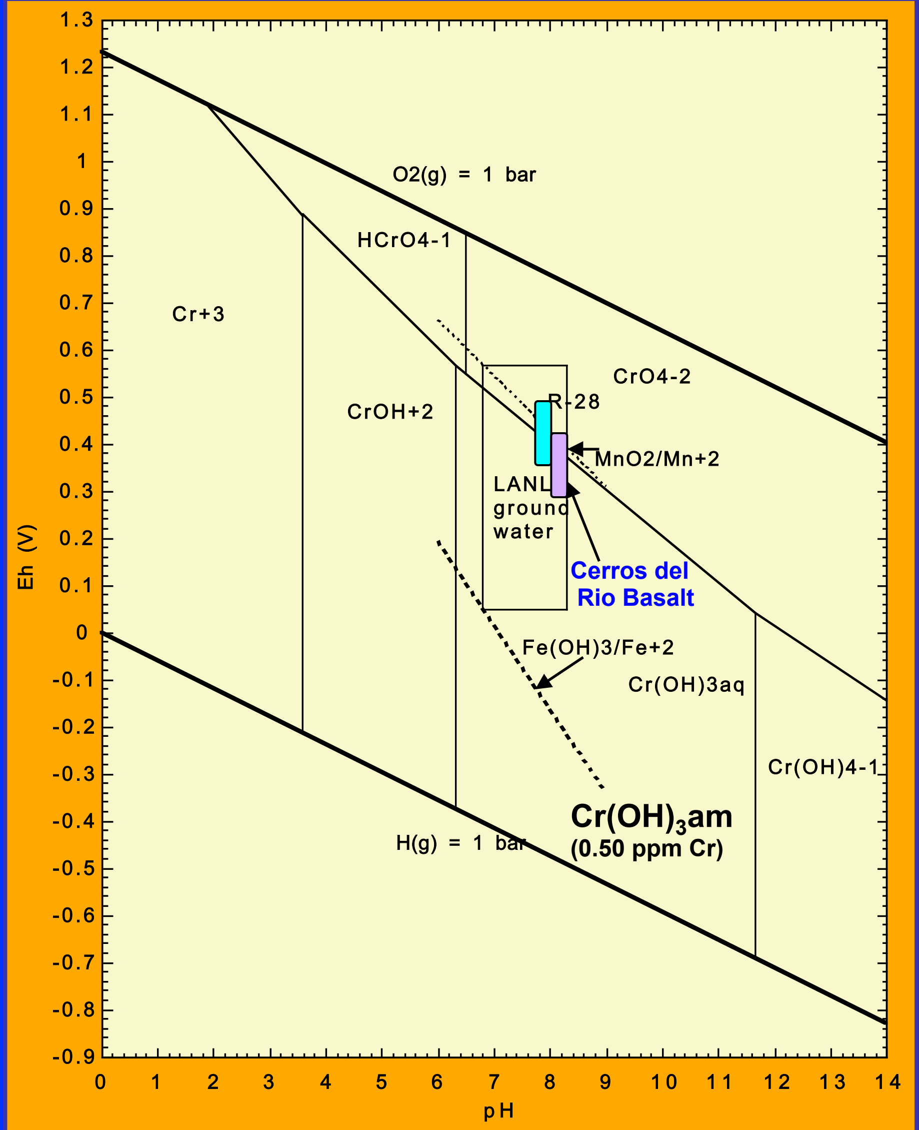
$Cr(OH)_3(am) + 3MnO_2(s) + H_2O = CrO_4^{2-} + 3MnOOH(s) + 2H^+$

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

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

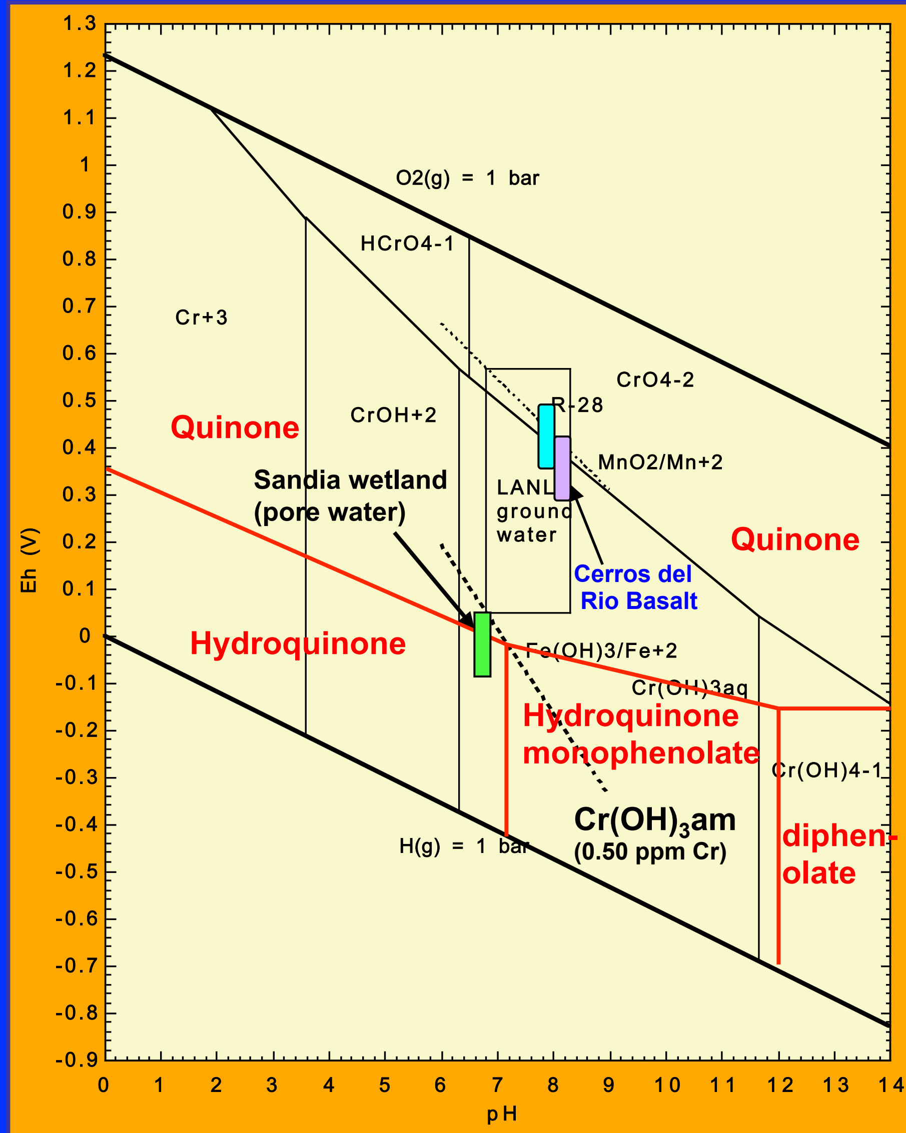
Cr Reduction:

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

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

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, respectiv

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

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

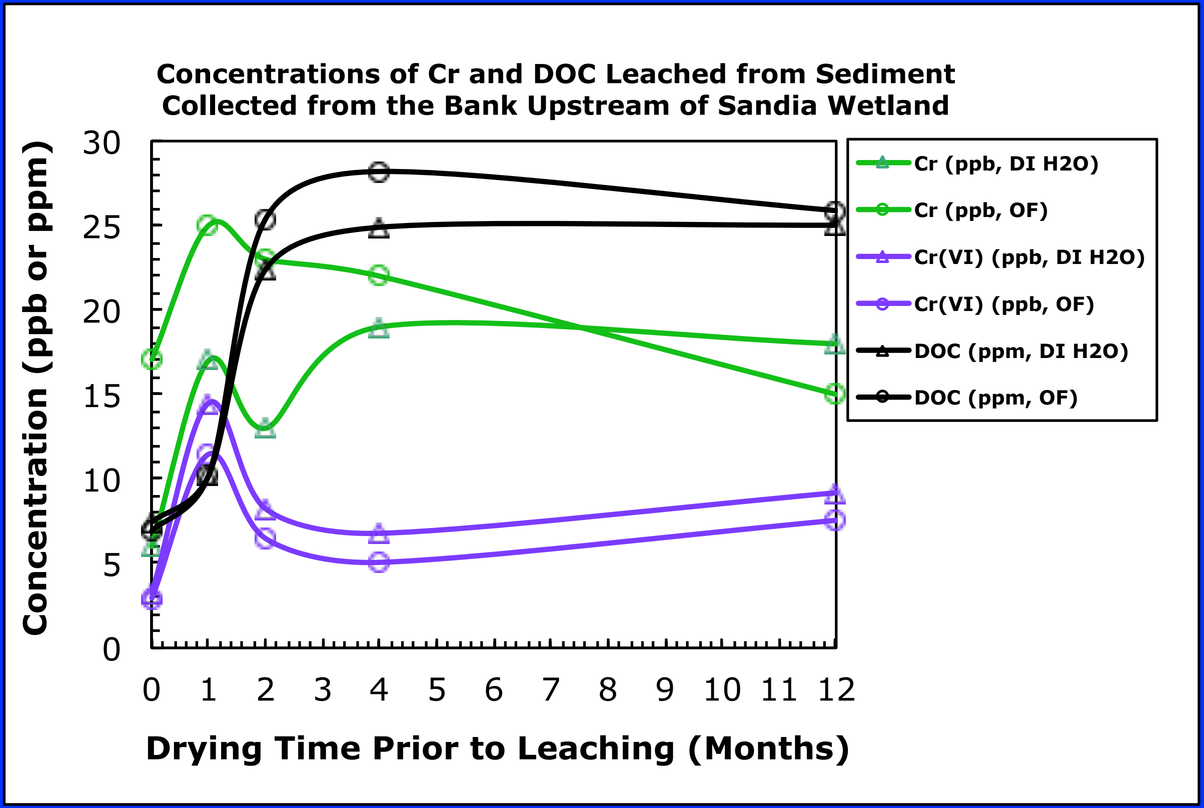
Under oxidizing conditions Mn(II) will oxidize to Mn(IV). Mn(IV) is then available to *potentially* reoxidize Cr(III) to Cr(VI) .

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

- 8 locations – sediment and organic rich materials
- Natural and oven drying
- 1, 2, 4, and 12 months
- DI H_2O and treated sewage effluent

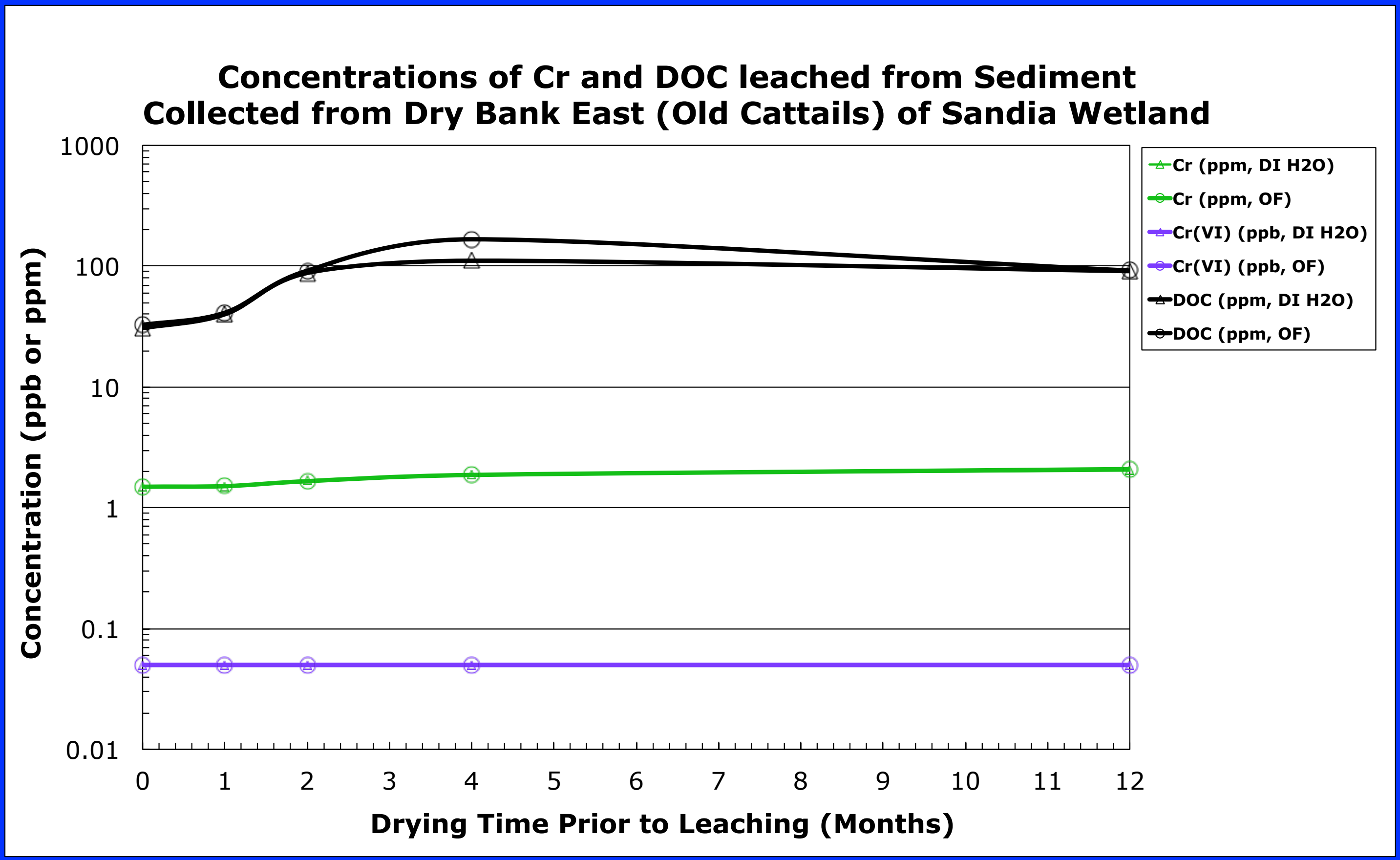
- Cr(VI) range – 0.06 to 14.5 ppb
- Analysis of Mn(IV) to Fe(II) to Cr(III) indicate stability of Cr(III)
- Agrees with observed stable mass of Cr(III) in wetland 35 yr after release

Results of Sandia Wetland Drying Experiments



Sample drying time (in months) prior to leaching versus concentrations of dissolved concentrations of 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.

Results of Sandia Wetland Drying Experiments



Sample drying time (in months) prior to leaching versus concentrations of dissolved concentrations of 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.

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)

$Fe^sOH + Cr^{3+} + H_2O - 2H^+ = Fe^sOOHCr^+$

3.72e-05 moles/L of hydrous ferric oxide (HFO) provides $10^{-6.92}$ moles of Fe^sOOHCr^+ 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).

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.
- Dissolved concentrations of Cr(VI) ranged from $10^{-8.9}$ M to $10^{-6.6}$ M (0.06 to 14.5 μg/L) in leachate samples analyzed as part of Sandia Canyon wetland drying experiments and agree with monitoring data.

Acknowledgements

Steve Reneau, Michael Rearick, Emily Kluk, and David Vaniman provided technical expertise in field and experimental studies.

SUPPLEMENTAL SLIDES

Additional Analytical Methods

Major Ions

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

Trace Elements

Inductively coupled plasma-optical emission spectroscopy and inductively coupled plasma-mass spectrometry

Background Concentrations of Total Dissolved Chromium in the Regional Aquifer, Los Alamos, New Mexico

- Eighty water samples analyzed using ICP-MS
- Mean: 5.90E-08 ± 3.10E-08 (1σ) M (3.07 ± 1.61 μg/L)
- Maximum: 1.38E-07 M (7.20 μg/L)
- Minimum: 7.50E-09 M (0.39 μg/L)

M denotes molar

Source: LANL 2007

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