Reduction of Cr Stable isotopes in contaminated groundwater in Leon Valley, Mexico

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NDSU Geochemistry 2018

Chromium

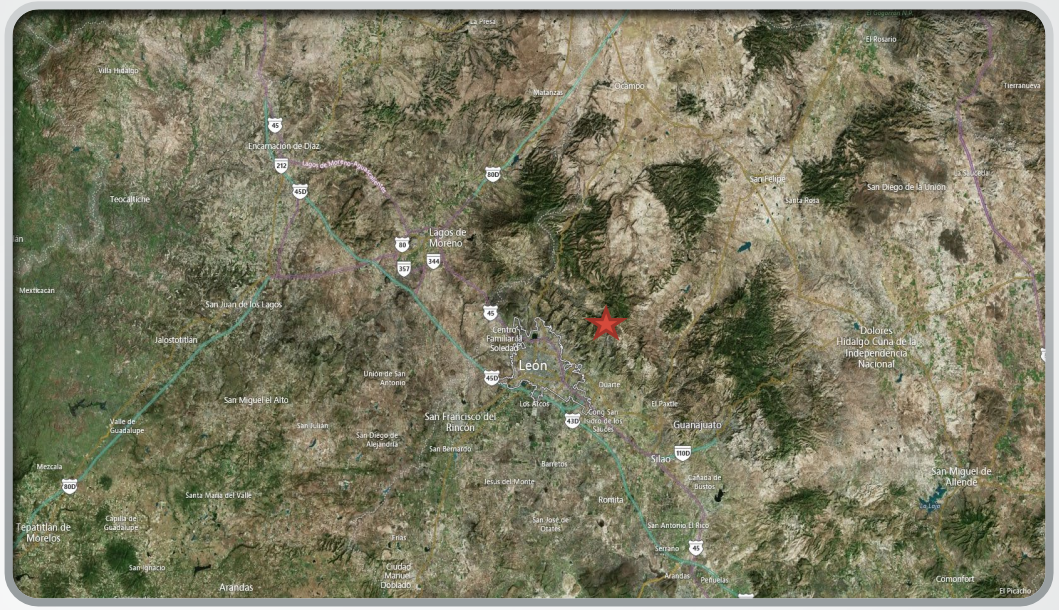
- Uses
  - Metallurgy
  - Dyes for paints
  - Synthetic rubies
  - Tanning
- Two main valences
  - Cr(III)
  - Cr(VI)

Chromium Toxicity

- Cr(III) poor mobility and less toxic
- Cr(VI) Highly mobile and toxic
  - 10-100 times more toxic (Gon Kim et al., 2002)
- Detected in 89% if tap water in U.S.A. (Branan, 2011)
- Top 17 chemicals posing a threat to humans

Leon Valley

- Basalts, and lacustrine sediments



Credit:

Top: Flickriver.com

Bottom: google maps

Previous Studies

- Detected in 1987
- International attention in 1994
- Buenavista

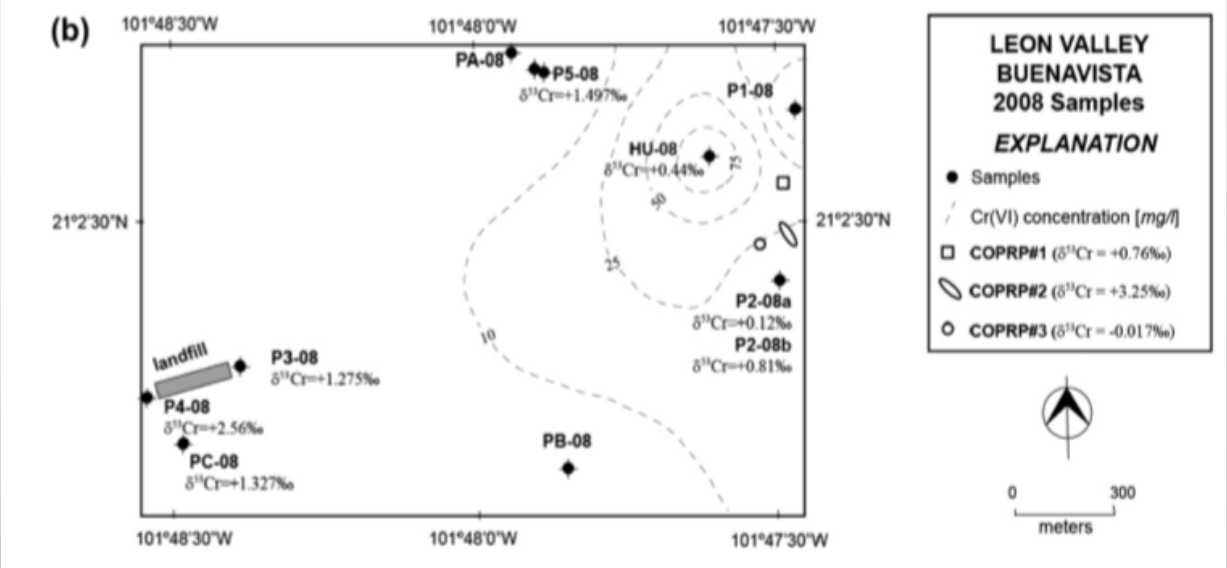
Cr (VI) historical monitoring Buenavista, Guanajuato.

Well/ Piezometer	Sampling depth (m)	Cr(VI) (in mg/L)	
		Median value (1991–1996)	Median value (2003–2005)
Hulera	–	**43.11**	**35.31**
Piezometer 2	8–12	**11.07**	**1.01**
	13–16	**12.67**	**6.37**
	17–19	**10.63**	**0.8881**
Piezometer 3	9–12	**0.0969**	<0.0052
	13–16	**0.1311**	0.0059
	17–20	**0.0542**	<0.0052
Piezometer 4	8–11	0.0316	<0.0052
	12–15	0.0200	0.0090
	16–20	0.0115	0.0061
Piezometer 5	8–11	**2.40**	<0.0052
	12–15	**1.89**	<0.0052
Cartonera	–	**11.79**	**15.87**

Alejandro V.A. et Al., 2012

Chromium sources

- 3 CORPS (Chromate Ore Processing Residue Piles)
- Natural sources
- Landfill



Alejandro V.A. et Al., 2012

Sampled values

Table 2
Sampling location and key chemical parameters.

Sample ID	Location	Coordinates LAT (N) LONG (W)		pH	Temp. (°C)	Cond. (mS/cm)	Alkalinity (HCO_3)	Total Cr (mg/L)	Cr(VI) (mg/L)	δ^{53} Cr (‰)	Red $_{calc}$ (%)[a]
Buenavista (BV)											
P3-07	Piezometer 3	21.03814	101.80638	7.01	22.75	371	199.25	0.030	0.010	–	–
PA-07	Piezometer A	21.04608	101.79892	7.04	24.46	747	266.50	–	0.033	+0.33	9.0
PC-07	Piezometer C	21.03567	101.80794	6.91	23.50	1.429	–	0.003	<0.001	–	–
CA-07	Cartonera well	21.04559	101.79804	7.09	26.81	870	228	**11**	10.84	−0.08	–
P3-08	Piezometer 3	21.03814	101.80638	7.07	23.04	552	238.15	0.003	<0.001	+1.275	30.5
P4-08	Piezometer 4	21.03690	101.80901	6.96	22.96	1238	489.44	**0.43**	0.42	+2.599	52.4
P5-08	Piezometer 5	21.04565	101.79825	7.09	22.31	990	246.23	**0.15**	0.14	+1.407	33.1
PA-08	Piezometer A	21.04608	101.79892	6.82	23.80	782	432.19	**0.08**	0.002	–	–
PC-08	Piezometer C	21.03567	101.80794	7.14	22.25	918	338.93	0.025	0.020	+2.327	48.6
Química Central (QC)											
P2-07	Piezometer 2	21.04025	101.79151	6.51	23.96	6800	931.50	**21.5**	10.80	+0.46	12.3
PB-07	Piezometer B	21.03592	101.79672	6.74	21.69	4300	647.88	0.009	0.005	–	–
HU-07	Hulera well	21.04333	101.79344	6.54	23.29	5140	354	**128**	121.57	+0.33	9.0
P1-08	Piezometer 1	21.04459	101.79103	6.74	23.11	3716	1193.25	<0.003	<0.001	–	–
P2-08A	P-B @ 13 m	21.04025	101.79151	6.51	23.96	2040	792.71	**62.13**	56.92	+0.124	3.5
P2-08B	P-B @ 26 m	21.04025	101.79151	6.49	23.50	8150	991.32	**19.7**	17.90	+0.811	20.7
PB-08	Piezometer B	21.03592	101.79672	6.84	20.91	3784	591.47	<0.003	<0.001	–	–
HU-08	Hulera well	21.04333	101.79344	6.60	30.84	4805	785.78	**95.1**	92.55	+0.440	11.8
COPRP-1	–	–	–	–	–	–	–	–	–	+0.76	20
COPRP-2	–	–	–	–	–	–	–	–	–	+3.25	60
COPRP-3	–	–	–	–	–	–	–	–	–	−0.017	–

Concentrations in bold exceed Mexican maximum drinking water contaminant levels (NOM 127-SSA1-1994, 2000).
[a] Calculated using Eq. (2).

Table 3
Analyses for major ions and trace metals.

Sample ID	Location	Ca (mg/L)	K (mg/L)	Na (mg/L)	Mg (mg/L)	Cl (mg/L)	NO_3 (mg/L)	SO_4^{2-} (mg/L)	Al (μg/L)	Ba (μg/L)	Fe (μg/L)	Mn (μg/L)	U (μg/L)
Buenavista (BV)													
P3-07	P3	34.1	14.3	34.05	8.5	3.82	<0.1	18.2	2	132	<10	6.6	<1.5
PA-07	PA	64.1	20.7	91.0	13.4	44.1	<0.1	66.8	3	173	<10	9	48
PC-07	PC	136	62.4	136.5	54.8	101.4	<0.1	214	3	<0.1	<10	<0.9	<1.5
CA-07	Cartonera	82.2	22.4	75.5	13.4	92.8	<0.1	45.1	29	<0.1	<10	<0.9	<1.5
P3-08	P3	54.1	15.1	31.7	10.1	30.35	**12.74**	19.9	48	254	<10	54	3
P4-08	P4	133.0	29.8	70.0	25.2	121.1	<0.1	145.5	2	116	<10	1	19
P5-08	P5	79.2	33.9	57.2	13.5	19.0	**61.35**	170.0	99	233	<10	4	3
PA-08	PA	111.9	25.9	78.1	10.9	45.7	<0.1	8.9	2	<0.1	**310**	77	<1.5
PC-08	PC	123.8	12.7	68.1	12.2	62.2	<0.1	104.6	7	148	<10	50	13
Química Central (QC)													
P2-07	P2	651.3	35	**866.7**	164	**1660**	<0.1	**549.3**	30	<0.1	<10	<0.9	<1.5
PB-07	PB	404.8	21.5	**473.8**	177.9	**860**	<0.1	**463.2**	3	164	<10	9	59
HU-07	Hulera	521	45	**582.4**	121.5	**1027.5**	<0.1	**522.3**	29	<0.1	<10	<0.9	<1.5
P1-08	P1	441.2	37.3	**968.1**	133.7	**1837.8**	<0.1	**470.0**	37	331	120	<0.9	18
P2-08A	P2 @ 13 m	263.0	30.3	**358.8**	63.6	**923.1**	<0.1	**926.6**	<2	125	<10	37	45
P2-08B	P2 @ 26 m	369.2	40.9	**749.4**	183.9	**3312.2**	<0.1	**613.3**	<2	117	<10	17	38
PB-08	PB	392.8	27.5	**247.7**	96.3	**1165.1**	9.86	397.3	26	368	<10	131	78
HU-08	Hulera	569.0	43.5	**491**	109.3	**1398.8**	<0.1	**458.8**	<2	57	<10	19	45

Concentrations in bold exceed Mexican maximum drinking water contaminant levels (NOM 127-SSA1-1994, 2000).

Alejandro V.A. et Al., 2012

Cr sampled data

Cr(2)	7.142e-21				
Cr+2	7.142e-21	2.896e-21	-20.146	-20.538	-0.392
Cr(3)	1.107e-03				
Cr3(OH)4+5	3.525e-04	1.977e-06	-3.453	-5.704	-2.251
Cr(OH)2+	3.749e-05	2.985e-05	-4.426	-4.525	-0.099
CrOH+2	1.066e-05	4.321e-06	-4.972	-5.364	-0.392
Cr(OH)3	5.180e-07	5.180e-07	-6.286	-6.286	0.000
Cr2(OH)2+4	4.942e-07	1.626e-08	-6.306	-7.789	-1.483
Cr+3	6.086e-08	1.248e-08	-7.216	-7.904	-0.688
Cr(OH)4-	8.968e-10	7.140e-10	-9.047	-9.146	-0.099
CrCl+2	4.947e-10	2.006e-10	-9.306	-9.698	-0.392
CrCl2+	1.137e-11	9.054e-12	-10.944	-11.043	-0.099
Cr(5)	6.409e-19				
CrO4-3	6.409e-19	7.793e-20	-18.193	-19.108	-0.915
Cr(6)	4.118e-17				
CrO4-2	2.801e-17	1.102e-17	-16.553	-16.958	-0.405
HCrO4-	1.318e-17	1.049e-17	-16.880	-16.979	-0.099
CrO3Cl-	9.954e-25	7.925e-25	-24.002	-24.101	-0.099
H2CrO4	1.262e-25	1.262e-25	-24.899	-24.899	0.000
Cr2O7-2	9.785e-33	3.851e-33	-32.009	-32.414	-0.405

Cr Species

	S.I.	Log IAP	log K	
Lopezite	-35.55	-53.09	-17.54	K2Cr2O7
Magnesiochromite	11.81	33.81	22.00	MgCr2O4
Na2Cr2O7	-40.19	-50.40	-10.20	Na2Cr2O7
Na2CrO4	-23.28	-20.36	2.92	Na2CrO4
Chromite	13.61	29.04	15.43	FeCr2O4
Cr	-54.38	44.96	99.33	Cr
CrCl3	-30.95	-12.84	18.11	CrCl3
CrO2	0.48	-18.75	-19.22	CrO2
CrO3	-26.48	-30.04	-3.55	CrO3
Eskolaite	15.60	6.41	-9.19	Cr2O3

Addition of O2

After addition of O2

Cr(2)	7.144e-21				
Cr+2	7.144e-21	2.896e-21	-20.146	-20.538	-0.392
Cr(3)	1.108e-03				
Cr3(OH)4+5	3.526e-04	1.977e-06	-3.453	-5.704	-2.251
Cr(OH)2+	3.749e-05	2.985e-05	-4.426	-4.525	-0.099
CrOH+2	1.066e-05	4.321e-06	-4.972	-5.364	-0.392
Cr(OH)3	5.179e-07	5.179e-07	-6.286	-6.286	0.000
Cr2(OH)2+4	4.943e-07	1.626e-08	-6.306	-7.789	-1.483
Cr+3	6.087e-08	1.248e-08	-7.216	-7.904	-0.688
Cr(OH)4-	8.965e-10	7.138e-10	-9.047	-9.146	-0.099
CrCl+2	4.949e-10	2.006e-10	-9.306	-9.698	-0.392
CrCl2+	1.138e-11	9.058e-12	-10.944	-11.043	-0.099
Cr(5)	6.408e-19				
CrO4-3	6.408e-19	7.790e-20	-18.193	-19.108	-0.915
Cr(6)	4.117e-17				
CrO4-2	2.800e-17	1.102e-17	-16.553	-16.958	-0.405
HCrO4-	1.317e-17	1.049e-17	-16.880	-16.979	-0.099
CrO3Cl-	9.954e-25	7.924e-25	-24.002	-24.101	-0.099
H2CrO4	1.262e-25	1.262e-25	-24.899	-24.899	0.000
Cr2O7-2	9.781e-33	3.848e-33	-32.010	-32.415	-0.405

Na2Cr2O7	-40.19	-50.40	-10.20	Na2Cr2O7
Na2CrO4	-23.28	-20.36	2.92	Na2CrO4

Original

Cr(2)	7.142e-21				
Cr+2	7.142e-21	2.896e-21	-20.146	-20.538	-0.392
Cr(3)	1.107e-03				
Cr3(OH)4+5	3.525e-04	1.977e-06	-3.453	-5.704	-2.251
Cr(OH)2+	3.749e-05	2.985e-05	-4.426	-4.525	-0.099
CrOH+2	1.066e-05	4.321e-06	-4.972	-5.364	-0.392
Cr(OH)3	5.180e-07	5.180e-07	-6.286	-6.286	0.000
Cr2(OH)2+4	4.942e-07	1.626e-08	-6.306	-7.789	-1.483
Cr+3	6.086e-08	1.248e-08	-7.216	-7.904	-0.688
Cr(OH)4-	8.968e-10	7.140e-10	-9.047	-9.146	-0.099
CrCl+2	4.947e-10	2.006e-10	-9.306	-9.698	-0.392
CrCl2+	1.137e-11	9.054e-12	-10.944	-11.043	-0.099
Cr(5)	6.409e-19				
CrO4-3	6.409e-19	7.793e-20	-18.193	-19.108	-0.915
Cr(6)	4.118e-17				
CrO4-2	2.801e-17	1.102e-17	-16.553	-16.958	-0.405
HCrO4-	1.318e-17	1.049e-17	-16.880	-16.979	-0.099
CrO3Cl-	9.954e-25	7.925e-25	-24.002	-24.101	-0.099
H2CrO4	1.262e-25	1.262e-25	-24.899	-24.899	0.000
Cr2O7-2	9.785e-33	3.851e-33	-32.009	-32.414	-0.405

Na2Cr2O7	-40.19	-50.40	-10.20	Na2Cr2O7
Na2CrO4	-23.28	-20.36	2.92	Na2CrO4

Increasing iron oxide

More iron oxide

Cr(2)	7.139e-21					
Cr+2	7.139e-21	2.892e-21	-20.146	-20.539	-0.392	(0)
Cr(3)	1.107e-03					
Cr3(OH)4+5	3.526e-04	1.970e-06	-3.453	-5.706	-2.253	(0)
Cr(OH)2+	3.745e-05	2.981e-05	-4.427	-4.526	-0.099	(0)
CrOH+2	1.065e-05	4.315e-06	-4.973	-5.365	-0.392	(0)
Cr(OH)3	5.173e-07	5.173e-07	-6.286	-6.286	0.000	(0)
Cr2(OH)2+4	4.943e-07	1.622e-08	-6.306	-7.790	-1.484	(0)
Cr+3	6.084e-08	1.246e-08	-7.216	-7.904	-0.689	(0)
Cr(OH)4-	8.958e-10	7.131e-10	-9.048	-9.147	-0.099	(0)
CrCl+2	4.943e-10	2.003e-10	-9.306	-9.698	-0.392	(0)
CrCl2+	1.135e-11	9.038e-12	-10.945	-11.044	-0.099	(0)
Cr(5)	6.412e-19					
CrO4-3	6.412e-19	7.783e-20	-18.193	-19.109	-0.916	(0)
Cr(6)	4.115e-17					
CrO4-2	2.799e-17	1.101e-17	-16.553	-16.958	-0.405	(0)
HCrO4-	1.316e-17	1.048e-17	-16.881	-16.980	-0.099	(0)
CrO3Cl-	9.941e-25	7.913e-25	-24.003	-24.102	-0.099	(0)
H2CrO4	1.260e-25	1.260e-25	-24.900	-24.900	0.000	(0)
Cr2O7-2	9.768e-33	3.841e-33	-32.010	-32.416	-0.405	(0)

Chromite	16.61	32.05	15.43	FeCr2O4

Original

Cr(2)	7.142e-21				
Cr+2	7.142e-21	2.896e-21	-20.146	-20.538	-0.392
Cr(3)	1.107e-03				
Cr3(OH)4+5	3.525e-04	1.977e-06	-3.453	-5.704	-2.251
Cr(OH)2+	3.749e-05	2.985e-05	-4.426	-4.525	-0.099
CrOH+2	1.066e-05	4.321e-06	-4.972	-5.364	-0.392
Cr(OH)3	5.180e-07	5.180e-07	-6.286	-6.286	0.000
Cr2(OH)2+4	4.942e-07	1.626e-08	-6.306	-7.789	-1.483
Cr+3	6.086e-08	1.248e-08	-7.216	-7.904	-0.688
Cr(OH)4-	8.968e-10	7.140e-10	-9.047	-9.146	-0.099
CrCl+2	4.947e-10	2.006e-10	-9.306	-9.698	-0.392
CrCl2+	1.137e-11	9.054e-12	-10.944	-11.043	-0.099
Cr(5)	6.409e-19				
CrO4-3	6.409e-19	7.793e-20	-18.193	-19.108	-0.915
Cr(6)	4.118e-17				
CrO4-2	2.801e-17	1.102e-17	-16.553	-16.958	-0.405
HCrO4-	1.318e-17	1.049e-17	-16.880	-16.979	-0.099
CrO3Cl-	9.954e-25	7.925e-25	-24.002	-24.101	-0.099
H2CrO4	1.262e-25	1.262e-25	-24.899	-24.899	0.000
Cr2O7-2	9.785e-33	3.851e-33	-32.009	-32.414	-0.405

Chromite	13.61	29.04	15.43	FeCr2O4

Work Summary

- Ran data tests in PHREEQC
  - Looking for drop in ratio between Cr3 and Cr6 from sampled value

Conclusions

- Results unsuccessful
  - Negligible change in amounts of Cr
- Need for methods not testable in PHREEQC

References

- Alejandro V.A., Andre S. Ellis, Maria A. Armienta, Ofelia Morton-Berma, Thomas M. Johnson, 2012, Geochemistry and Cr Stable isotopes of Cr-contaminated groundwater in Leon valley, Guanajuato, Mexico.
- Wikipedia