

Texas Commission on Environmental Quality

INTEROFFICE MEMORANDUM

To: TARA Staff
Remediation Division Staff

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Subject: Chromium (Cr)

1. Introduction:

The PCL Tables for TRRP and the MSC Tables for the Risk Reduction Rules contain values for Chromium as Cr^{3+} and Total Chromium, and for Cr^{6+} as a separate listing. During assessments, chromium concentrations in soil and groundwater are typically being analyzed as Total Chromium. Without speciation of chromium, the person is assuming the more toxic forms of chromium, Cr^{6+} are not present at the affected property. This assumption may be unfounded.

This memorandum provides guidelines for addressing this matter.

2. Anthropogenic Sources of Chromium:

The metal chromium is used mainly in the manufacture of steel and other alloys. Chromium compounds, in either the Cr (III) or Cr (VI) forms, are used for chrome plating, the manufacture of dyes and pigments, leather and wood preservation, and treatment of cooling tower water. Smaller amounts are used in drilling muds, textiles, and toner for copying machines.

Cr (VI), which, along with the less common metallic chromium [Cr (0)], is most commonly produced by industrial processes. Air emissions of chromium are predominantly of Cr (III), and in the form of small particles or aerosols. The most important industrial sources of chromium in the atmosphere are those related to ferrochrome production. Ore refining, chemical and refractory processing, cement-producing plants, automobile brake lining and catalytic converters for automobiles, leather tanneries, and chrome pigments also contribute to the atmospheric burden of chromium. Dermal exposure to chromium may occur during the use of consumer products that contain chromium, such as wood treated with copper dichromate or leather tanned with chromic sulfate.

Some Cr (VI) mineral phases identified in sludge from metal plating-contaminated sites include crocite (PbCrO_4), iranite ($\text{PbCrO}_4 \cdot \text{H}_2\text{O}$), and tarapacaitite (K_2CrO_4). Cr (VI) also has been observed to exist as a complete solid solution of BaCrO_4 - BaSO_4 .



3. Recommended Methodology for Cr Releases to Groundwater:

GW ingestion PCLs for Cr (III) and Cr (VI) are the same because they are based on the federal MCL for *Total Cr* of 0.1 mg/L (40 CFR 141.51), to which TRRP defaults. Therefore, no Cr speciation is necessary for the purpose of evaluating the *groundwater ingestion* pathway.

No predictable relationship between concentrations of Cr (III) and concentrations of Cr (VI) in groundwater exists. While equilibrium conditions may be estimated, actual reaction kinetics likely will always lag behind. At best, gross conclusions about the dominant Cr oxidation state can be made on a relative basis (*see* Appendix A). However, given site conditions, it is not possible to ascribe relative proportions of Cr species based on Total Chromium concentrations.

4. Recommended Methodology for Cr Releases to Soil:

TRRP lists separate soil PCLs for Cr (III) and Cr (VI), with a designation of "total chromium" provided parenthetically under the Cr (III) PCL. While it may be appropriate to apply the Cr (III) PCL to a measured total chromium measurement in some situations (*e.g.*, low level releases to soil from sources not typically associated with hexavalent chromium), this designation is not meant to take the place of a site-specific evaluation as to whether Cr (VI) should be analyzed as a separate COC at a given site.

The analysis of Cr species in soils is not difficult. However, soil samples destined for Cr speciation analysis must remain *field moist*, and not be air-dried, thus requiring special handling and preservation protocols. (*See* Appendix B for additional information on Cr in soils.)

In lieu of a convenient and reliable screening scheme, the following methodology is recommended for the determination of the potential threat posed by Cr (VI) in groundwater.

1. Review site history for activities which are known to produce Cr wastes (see examples above).
2. Soil associated with sites at which Cr wastes are known to have been generated should be analyzed specifically for Total Cr and Cr (VI) for the purpose of evaluating relative Cr species content.
3. Analysis of Cr (VI) should be performed in accordance with the standard method provided in Table I.
4. Cr (VI) concentrations then can be compared to the Cr (VI) PCLs.

The recommended analytical method for the analysis of Cr (VI) in soils is presented in Table I.

Table I
Recommended Method for the Analysis of Cr (VI) in Soils

Analyte	Application	Analytical Method	Analytical Description	Range
Cr (VI)	Aqueous extracts of soil	SSSA, 1996	APDC chelation; colorimetry	> 5.2 µg/L (in extract)

APDC = ammonium pyrrolidine dithiocarbamate

5. Recommended Methodology for Cr Releases to Surface Water:

TRRP 24 (*Determining PCLs for Surface Water and Sediment*) discusses the methodology for Cr assessments in surface water. TRRP-24 is consistent with the TCEQ *Procedures to Implement the Texas Surface Water Quality Standards (2002)* in which the Texas Surface Water Quality Standards (TSWQS) requires the person to report concentrations of total recoverable Cr, dissolved Cr (III), and dissolved Cr (VI). These concentrations can be determined using two (2) separate analyses of surface water, one for dissolved Cr (VI), the other for total recoverable Cr. Hence, for the *groundwater-to-surface water* pathway, groundwater samples must be collected and analyzed for dissolved Cr (VI) and total recoverable Cr.

The following algorithm is used to differentiate the Cr fractions:

$$\text{Total recoverable Cr} = \text{dissolved Cr (VI)} + \text{adsorbed Cr (VI)} + \text{dissolved Cr (III)} + \text{adsorbed (III)}$$

NOTE: For purposes of surface water assessments, the TCEQ assumes the amount of adsorbed Cr (VI) is negligible, allowing the calculation of total Cr (III) to be performed as follows:

$$\text{Total Cr (III)} = \text{total recoverable Cr} - \text{dissolved Cr (VI)}$$

Surface water samples collected for analysis of dissolved metals should be *filtered in the field*. Contract laboratories can provide in-line 0.45 µm filter kits.

Table II summarizes the analytical methods for dissolved and total recoverable Cr in drinking and natural waters.

**Table II
Recommended Methods for the Analysis of Dissolved and Total Recoverable Cr**

Analyte	Application	Analytical Method	Analytical Description	Range
Total Cr	Drinking, surface, groundwater and saline water	EPA 7190	AA, direct aspiration	5 - 100 µg/L
Total Cr	Groundwater, aqueous samples	EPA 6010B	ICP-AES	> 5 µg/L
AA = Atomic Absorption spectrophotometry ICP-AES = Inductively Coupled Plasma - Atomic Emission Spectroscopy				

Table III summarizes recommended analytical methods for dissolved hexavalent chromium [Cr (VI)]. Generally, EPA Method 218.4 is the preferred analytical method for dissolved Cr (VI). The holding time for water samples destined for dissolved Cr (VI) analysis is 24 hours.

Table III
Recommended Methods for the Analysis of Dissolved Cr (VI)

Analyte	Application	Analytical Method	Analytical Description	Range
Dissolved Cr (VI)	Drinking, surface, and saline water	EPA 218.4	APDC chelation, AA	10 - 250 µg/L
Dissolved Cr (VI)	Drinking and surface water; filtered domestic and industrial waste	EPA 218.5	Pb precip., AA	5 - 100 µg/L
Dissolved Cr (VI)	Drinking, groundwater and industrial wastewater effluent	EPA 218.6	Column separation, DPC, IC	Lab-specific
Dissolved Cr (VI)	Water and brines	USGS I-1232	APDC chelation, AA	1 - 25 µg/L (higher with dilution)
Dissolved Cr (VI)	Water and brines; Fe > 5,000 µg/L	USGS I-1230	APDC chelation; colorimetry	50 - 4,000 µg/L

APDC = ammonium pyrrolidine dithiocarbamate
 AA = Atomic Absorption spectrophotometry
 DPC = Diphenylcarbazide
 IC = Ion Chromatography

6. References:

SSSA 1996 Chromium, *in Methods of Soil Analysis. Part 3. Chemical Methods*, Soil Science Society of America Book Series 5, American Society of Agronomy, Madison, WI, p. 683 - 701.

APPENDIX A

Aqueous Geochemistry of Chromium

Aqueous (dissolved) Cr exists in the +2, +3, and +6 oxidation states. However, only the +3 [Cr (III)] and the +6 [Cr (VI)] species are found in the environment. Figure 1 is a generalized Eh-pH diagram for the Cr - H₂O system. Cr (III) exists over a wide range of Eh and pH conditions. Cr (VI) exists only in strongly oxidizing conditions.

Table A-1 summarizes the dominant Cr species that exist under various aqueous conditions.

Generally, groundwater plumes containing high concentrations of Cr is more likely to be comprised of Cr (VI) than Cr (III) because Cr (III) is more likely to have precipitated as Cr₂O₃·xH₂O and, to a lesser extent, adsorbed. Cr (VI) is highly mobile in groundwaters with neutral to basic pH. In acidic groundwaters Cr (VI) can be moderately adsorbed by pH-dependent minerals such as Fe- and Al-oxides.

Under favorable conditions, Cr (VI) reduces to Cr (III) rapidly via ferrous iron, organic matter, and microbes. The oxidation of Cr (III) to Cr (VI) by dissolved oxygen and Mn-oxides is kinetically slower. Redox conditions and pH dominate Cr speciation.

Table A-I summarizes the dominant aqueous Cr ions likely to exist in equilibrium with various aqueous conditions.

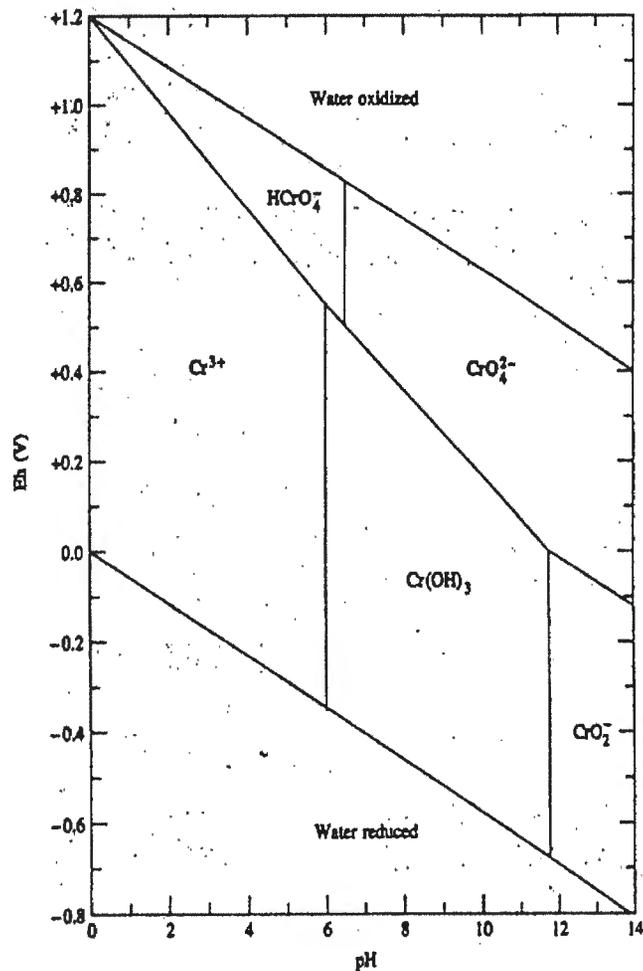


Figure 1: Eh - pH diagram for Cr species.

TABLE A-I
Dominant Cr Ions Stable in Various Aqueous Conditions

Cr Oxidation State	Aqueous Conditions	Dominant Aqueous Cr Species
Cr (III)	pH < 3.5	Cr ³⁺
	pH > 3.5	CrOH ²⁺
	increased pH	Cr(OH) ₂ ⁺
	increased pH	Cr(OH) ₃ ⁰ (Aq)
	increased pH	Cr(OH) ₄ ⁻
	Higher Cr concentrations	Cr ₂ (OH) ₂ ⁴⁺
	Higher Cr concentrations	Cr ₃ (OH) ₄ ⁵⁺
Cr (VI)	pH < 6.5 & Conc < 30 mM	HCrO ₄ ⁻
	pH < 6.5 & Conc > 30 mM	Cr ₂ O ₇ ²⁻
	pH > 6.5	CrO ₄ ²⁻

APPENDIX B Chromium in Soil

Cr (III) is cationic in the pH range of most surface soils [like Fe (III) and Al (III)]. Cr (III) is precipitated by OH⁻ at pH values > 4 to 5.5. Cr (III) forms "... thermodynamically stable and kinetically inert" complexes with organic and inorganic ligands that may or may not be soluble, depending on compound and soil pH. Most Cr (III) is insoluble in near-neutral soils as paracrystalline Cr(OH)₃ or more crystalline forms, such as Cr₂O₃. The relative insolubility of Cr (III) is responsible for its low soil - soil water partitioning capacity (K_d).

The sequestration of Cr (III) into the solid phase is significantly higher than that of Cr (VI). However, the sequestration processes include not only sorption to existing mineral phases in soil, but also *precipitation* of Cr-bearing phases (*e.g.*, amorphous iron oxides, *etc.*). Additionally, the large variance of K_d values with pH [30 TAC §350.73(e)(1)(C)] is a function of the pH-depend isoelectric points of various minerals.

Some forms of Cr (III) may oxidize to the more soluble form of Cr (VI) via inorganic and organic mediates. Cr (III) can readily oxidize to Cr (VI) by reactions involving Mn (III, IV) (hydro)oxides.

Table B-I summarizes the prevalent Cr species in soils.

**TABLE B-I
Prevalent Cr Species in Soils**

Cr Oxidation State	Acidic Soils	Alkaline Soils
Cr (III)	CrOH ²⁺	Cr(OH) ₄ ⁻
Cr (VI)	CrO ₄ ²⁻	CrO ₄ ²⁻

Cr (III) compounds typically are less soluble than Cr (VI) compounds. Table B-II summarizes the solubilities of some common Cr compounds.

TABLE B-II
Solubilities of Some Cr Compounds

Compound	Formula	CAS No.	Aqueous Solubility (g/100 mL)	@ T (°C)
Ammonium chromate	$(\text{NH}_4)_2\text{CrO}_4$	7788-98-9	40.5	30
Calcium chromate	CaCrO_4	13765-19-0	2.23	20
Chromic acid	CrO_3	1333-82-0	61.7	0
Potassium chromate	K_2CrO_4	7789-50-6	62.9	20
Potassium dichromate	$\text{K}_2\text{Cr}_2\text{O}_7$	7789-50-9	4.9	0
Sodium chromate	Na_2CrO_4	7775-11-3	87.3	30
Sodium dichromate dihydrate	$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	7789-12-0	230	0