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ENVIRONMENTAL RESEARCH BRIEF

Effect of Chlorine on Chromium Speciation in Tap Water

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Abstract

The 24-hr oxidation of trivalent chromium to hexavalent chromium is reported in pH 5, 6, 7, and 8 chlorinated tap water with low levels of alkalinity, chloride, sulfate, and total organic carbon (TOC). The applicability and use of analytical methods for hexavalent chromium in the presence of chlorine are discussed.

Introduction

Chromium may occur in various forms in natural waters as a result of the weathering of bedrock and soils or the discharge of chromium-bearing wastes from sources such as tanneries, cooling towers, animal glue manufacturers, metal dipping, pickling and electroplating industries, and sewage treatment plants. The origin, occurrence, and fate of chromium in water and the oxidation-reduction processes controlling its speciation during transport and storage have been the topic of many investigations during the last decade.

In nature, chromium generally occurs as the stable mineral chromite (FeO·Cr₂O₃); it is usually immobilized in the trivalent form in bedrock and most soils (1). However, Bartlett and James (2) have reported the oxidation of trivalent chromium [Cr(III)] to hexavalent chromium [Cr(VI)] in many soils containing manganese. Robertson (3) cited the occurrence of Cr(VI) at levels exceeding 0.05 mg/L in ground water in Paradise Valley, Maricopa County, Arizona. Osaki et al. (4) investigated the speciation of chromium in the Muromi River of Japan and reported high concentrations of Cr(VI) in the spring and streams of the river's headwaters as a result of oxidation in the groundwater sources. Downstream and in the reservoir, the Cr(III) level

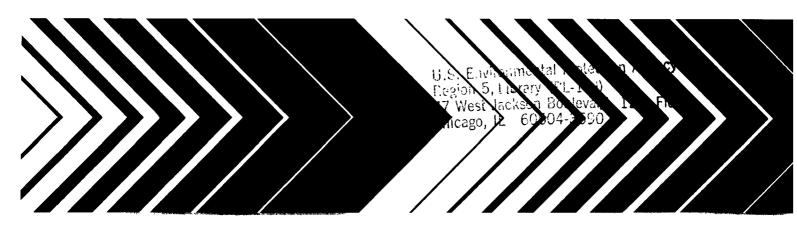
increased because the rate of reduction of Cr(VI) by humic substances was faster than the rate of oxidation of Cr(III) by dissolved oxygen. While studying the Columbia River, Cranston and Murray (5) observed that 98 percent of the chromium was in the hexavalent form. An interesting transport study by Canter and Gloyna (6) revealed that hexavalent chromium predominated in the non-polluted river but was reduced to the trivalent form when exposed to organic pollution. Schroeder and Lee (7) studied chromium speciation in simulated natural waters and reported that Cr(VI) was reduced by divalent iron [Fe(II)], dissolved sulfides, and certain organic compounds with sulfhydryl groups. They also noted that Cr(III) was oxidized by a large excess of manganese dioxide (MnO₂) at a slower rate by oxygen under conditions approximating those in natural waters. The factors controlling chromium speciation in natural waters were summarized by Florence and Batley (1) as follows:

- 1. oxygen content and redox potential of the water,
- presence of dissolved or particulate organic matter, and
- 3. presence of suspended inorganic matter.

Chromium speciation in biological systems has also been investigated during the last decade. Trivalent chromium appears to be the predominant species in cells, and its essential role in maintaining glucose, lipid, and protein metabolism in mammalian systems has been reported (1, 8, 9). Hexavalent chromium, however, appears to diffuse through cell membranes, oxidize, and then bind with other biochemical molecules to produce carcinogenic and mutagenic effects (1, 9):

Cognizant of these of these previous studies, reporting the toxicity of hexavalent chromium and the conversion potential of trivalent chromium in nature, the U.S. Environmental Protection Agency (EPA) has been reviewing the

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applicability of the current drinking water regulation for chromium. The advisability of changing the regulation from a single maximum contaminant level (MCL) basis (total chromium concentration) to a dual MCL basis (separate MCL for each of the two valence states) is being considered (10). To provide a fuller understanding of the potential trivalent chromium conversion to hexavalent chromium during and after drinking water treatment, two research investigations of the effects of chlorination on chromium speciation in water were conducted. One study, performed extramurally by Clifford and Chau (11), investigated the effects of chlorination on chromium speciation in natural waters and other matrices containing sodium chloride (NaCl), ammonia (NH₃) and humics. A report of this study is in preparation. Another study was conducted inhouse to determine the effects of 2 mg/L free residual chlorine on the speciation of 0.5 mg/L Cr(III) added to Cincinnati tap water at initial pH levels of 5, 6, 7, and 8. The approach, observations, conclusions, and recommendations of the latter study are reported here

Approach

General Study Design

A large aliquot of Cincinnati tap water was collected, and its free residual chlorine (FRC) concentration was adjusted to approximately 2 mg/L. Two 1-L aliquots of this chlorine-adjusted tap water were transferred to 1-L cubitainers and forwarded to the laboratory for physical and chemical characterization (alkalinity, arsenic, barium, cadmium, calcium, chloride, total chromium, color, specific conductance, copper, fluoride, iron, lead, magnesium, manganese, mercury, pH, total filterable residue or total dissolved solids, selenium, silver, sodium, sulfate, turbidity and zinc).

Four exposure study test solutions were prepared by transferring 2-L aliquots of chlorine-adjusted tap water to individual containers, adjusting the pH levels to pH 5, 6, 7, and 8, respectively, adding sufficient Cr(III) to achieve an approximate concentration of 0.5-mg/L and then quickly readjusting the pH levels as necessary. Each of the four test solutions was then divided into two portions. The first liter was labeled "initial sample" and immediately subjected to analysis for alkalinity, total and hexavalent chromium, FRC, pH, and TOC. The second portion of each of the test solutions was transferred to an individual 1-L, ground-glass-stoppered bottle, labeled "final sample," and set aside in the dark at room temperature for about 24 hr before analyses were initiated for dissolved oxygen and the aforementioned six characteristics. The details of the sample collection and preservation, reagent and test solution preparation, and analytical methodology are presented in the following section.

Analytical Approach

The study of the effect of chlorine on the speciation of chromium in Cincinnati tap water was conducted using the facilities, materials, and equipment of the Inorganics and Particulate Control Branch, Drinking Water Research Division, Water Engineering Research Laboratory.

Reagents, Equipment, and Analytical Methods—

During the exposure study of the four test solutions and all the related analyses, the laboratory glass and plastic wares were first cleaned using 1.1 nitric acid (HNO₃) and then rinsed liberally with deionized distilled water. All test solutions and analytical reagents were prepared using A C.S. reagent grade chemicals and deionized distilled water unless otherwise specified. All samples were collected, preserved, and analyzed according to the specifications in the analytical methods cited in Table 1.

Preparation of Test Solutions-

The preparation of the special test solutions for the exposure study was initiated by filling a 5-gal Nalgene®* jug with Cincinnati tap water (pH ~8.05). Sufficient saturated chlorine solution, freshly prepared by bubbling gaseous chlorine into deionized distilled water, was immediately added to the jug contents to raise the FRC concentration from 1.37 to 2.04 mg/L. Both FRC levels were determined amperometrically using the Penwalt Wallace & Tiernan Series A790 Titrator Four 2-L aliquots of this chlorineadjusted Cincinnati tap water were transferred from the 5-gal jug to individual 3-L beakers, and the pH levels were quickly adjusted to pH 5, 6, 7, and 8, respectively, using either 1 N sulfuric acid (H₂SO₄) or 1 N sodium hydroxide (NaOH) All pH measurements were performed using an Orion Model 801 Research Ionalyzer pH Meter equipped with a Metrohm Model AG9100 combination pH electrode and calibrated using fresh prepared Beckman Altex pH 4 and 6.86 buffers. Then 20 mL of a freshly prepared chromium chloride (CrCl $_3$) solution containing 50 mg/L Cr(III) was added to each 2-L aliquot, and any additional pH adjustment required to maintain the pH 5, 6, 7, or 8 levels was quickly made using 1 N H₂SO₄ or 1 N NaOH. The increase in each solution volume with the addition of chromium solution and pH adjustment solution was ≤ 1.05 percent and neglected in subsequent calculations.

Total Chromium Analyses—

All analyses for total chromium were performed by flameless atomic absorption technology using a Perkin Elmer Model 4000 Atomic Absorption Spectrometer, equipped with a Perkin Elmer Model 400 HGA Furnace, AS-40 Autosampler, background corrector, chromium hollow cathode lamp, nonpyrolyzed graphite tubes, argon gas, a 3579-nm wavelength, and a 0.7-nm slit. The procedural steps and operating conditions are presented in Table 2. The instrument was calibrated using six standard solutions containing 0, 5, 25, 50, 75, and 100 μ g/L Cr(VI) These were prepared by appropriate dilution of aliquots of a stock Cr(VI) solution (0.1414 g $K_2 Cr_2 O_7/L)$ and preserved with 1.5 mL concentrated HNO₃/L. After electrothermal atomization, the absorption response of a 20- μ L aliquot of each of the six solutions was observed, and a calibration plot relating absorption response and Cr(VI) concentration was prepared. The total chromium concentration of each initial and final test solution sample was then determined by electrothermally atomizing 20 μ L of a 1.5 dilution thereof, observing the absorption response, deriving the corresponding chromium concentration from the calibration plot, and multiplying by the appropriate dilution factor.

^{*}Mention of trade names or commercial products does not constitute endorsement or recommendation for use

Table 1.	Analytica	I Methods Used	in Sample Anal	vsis

Characteristic	Method	Reference	Comments
Alkalınıty	Potentiometric	SM 403*	Automatic titration to carbonate equivalence point
Arsenic	Flameless atomic absorption	EPA 206 2**	
Barıum	Atomic absorption, direct aspiration	EPA 208 1	NaCl substituted for KCl in reagents
Cadmium	Flameless atomic absorption	EPA 213 2	Instrumental parameters modified
Calcium	Atomic absorption, direct aspiration	EPA 215 1	
Carbon, total organic	UV promoted, persulfate oxidation	SM(16) 505B†	With DC 54 Xertex Dohrmann instrument
Chloride	Potentiometric, modified	SM407C	Automatic titration using silver, specific ion electrode
Chlorine, free residual	Amperometric titration	SM 408C	
Chromium, total	Flameless atomic absorption	EPA 218 2	
Chromium, hexavalent	Revised diphenylcarbazide colorimetric	SW 7196#	With standard additions§
Chromium, trivalent	Calculation		Difference between total and hexavalent chromium
Color	Visual comparison	SM 204A	With Hellige glass reference discs
Conductance, specific	Wheatstone bridge	EPA 1201	
Copper	Atomic absorption, direct aspiration	EPA 220 1	
Fluoride	Complexone	SM 413E	
Iron	Atomic absorption, direct aspiration	EPA 236 1	
Lead	Flameless atomic absorption	EPA 239 2	
Magnesium	Atomic absorption, direct aspiration	EPA 242 1	
Manganese	Atomic absorption, direct aspiration	EPA 243 1	
Mercury	Manual cold vapor	EPA 245 1	
Oxygen, dissolved	Membrane electrode	EPA 360 1	
рН	Electrometric	EPA 150 1	
Residue, total filterable (total dissolved solids)	Gravimetric	SM 209C	
Selenium	Flameless atomic absorption	EPA 270 2	
Silver	Atomic absorption, direct aspiration	EPA 272 1	
Sodium	Atomic absorption, direct aspiration	EPA 273 1 SM 325B	
Sulfate	Turbidimetric	EPA 375 4	

Table 1. (Continued)

Characteristic	Method .	Reference	Comments
Turbidity	Nephelometric	EPA 180 1	
Zinc	Atomic absorption, direct aspiration	EPA 289 1	

^{*}SM refers to American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater. 15th edition, unless otherwise specified. American Public Health Association, Washington, DC. 1981

Table 2. Conditions for Electrothermal Atomization of Chromium

Step No	Temp (C)	Ramp Time (sec)	Holding Time (sec)	Argon Flow Setting
1	100	10	10	Regular
2	130	2	20	Regular
3	1000	10	30	Miniflow
4	2700	1	6	Miniflow

Hexavalent Chromium Analyses—

The hexavalent chromium content of each initial and final test solution was determined by applying the standard additions technique to the revised diphenylcarbazide colorimetric procedure (see Table 1). Three 100-mL aliquots of each initial sample and three 50-mL aliquots of each final sample were processed. To the second and third aliquots in each set of three were added 0.5 and 1.0 mL, respectively, of a $4-\mu g/mL$ hexavalent chromium ($K_2Cr_2O_7$) solution. The effective Cr(VI) levels in the second and third aliquots of the initial and final samples were consequently 0.02 and 0.04 mg/L and 0.04 and 0.08 mg/L, respectively. All aliquots were then diluted to 101 mL, 2 mL of color reagent (250 mg 1,5-diphenylcarbazide in 50 mL A.C.S. reagent grade acetone) was added, and the pH was adjusted to 2 0 with 50% sulfuric acid (required volume \leq 0.5 mL). The absorbance of each processed aliquot was determined after 15 min against that of a reagent blank at 540 nm using a Beckman B Spectrophotometer equipped with a matched set of 5-cm cells. The absorbances of each set of three aliquots were then plotted versus the corresponding amounts of added Cr(VI) and the linearity of the plot checked. The Cr(VI) concentration of each test sample was then calculated by a linear regression analysis of the data and checked by graphical extrapolation.

Quality Assurance

All laboratory analyses were conducted using the control measures recommended in the EPA's analytical quality control manual (12). Accuracy was periodically evaluated by determining the percent recovery of analyte from

reference samples or from test samples spiked with known quantities of analyte. Precision was similarly determined periodically by replicate determinations of analyte, sample volume permitting. Appropriate Shewhart control charts and limits were established and maintained

Results and Discussion

Total and Hexavalent Chromium Method Evaluation and Quality Control

Before initiating the study of the effect of chlorine on the speciation of chromium in Cincinnati tap water, the applicability of the methods for determining hexavalent and total chromium was evaluated First applied was EPA $method\,218.5\,(13),\,a\,flameless\,atomic\,absorption\,technique$ for determining dissolved hexavalent chromium after coprecipitation. Unfortunately, the time this approach required to isolate and wash the coprecipitate of lead chromate/lead sulfate exceeded 1 hr. Consequently, the chlorine action on the trivalent chromium could not be stopped with sufficient speed or control. The timing of the diphenylcarbazide colorimetric method for hexavalent chromium (14), however, proved to be satisfactory, since only 15 to 30 min elapsed between sample aliquoting and initiation of color development. The absorbance of the developed color, however, was dependent on the concentration of free residual chlorine. A study of samples containing 0.05 mg/L Cr(VI) in the presence of 0, 0.5, 1.0, and 2.1 mg/L FRC revealed a 5% color depression with 1 mg/L chlorine and a significant 15% color depression with 2.1 mg/L chlorine. Since the 2-mg/L FRC contents of the proposed study test solutions might decrease variably with the degree of reaction with the trivalent chromium, the method of standard additions, as outlined previously, was applied to the colorimetric procedure to ensure accurate hexavalent chromium observations. Solutions containing 0.05 mg/L Cr(VI) in the presence of 0, 0 5, 1.0, and 2.1 mg/L FRC were analyzed to verify the applicability of this approach. The chromium additions to the second and third sample aliquots in each analysis set were equivalent to 0 10 and 0.20 mg/L, respectively. In each case the observed hexavalent chromium concentration was 0.05 mg/L. The accuracy of the approach was thus validated. A solution containing 0.5 mg/L Cr(III) was also subjected to hexavalent

^{**}EPA refers to Environmental Monitoring and Support Laboratory Methods for Chemical Analysis of Water and Wastes EPA/600/4-79/020 U.S. Environmental Protection Agency, Cincinnati, OH. March 1983

[†]SM(16) refers to previously cited SM reference, but 16th ed., 1985

[#]SW refers to Office of Solid Waste and Environmental Response Test Methods for Evaluating Solid Waste Physical/Chemical Methods SW-846 2nd ed U.S. Environmental Protection Agency, Washington, DC. July 1982

[§]See discussion in Trace Analysis, Spectroscopic Methods for Elements J W Winefordner, ed Vol 46 of Chemical Analysis John Wiley & Sons, New York, NY 1946 pp 41-42.

chromium analysis using the standard additions approach with the colorimetric procedure. The Cr(VI) additions to the second and third sample aliquots in this analysis set were equivalent to 0.02 and 0.04 mg/L, respectively. The observed hexavalent chromium concentration was 0.0008 mg/L, and confirmed both the specificity of the hexavalent chromium method and the trivalent chromium speciation in the CrCl₃ used in preparing the study test solutions.

A flameless atomic absorption technique, EPA method 218.2 (12), was used for determining total chromium. Two reference solutions were analyzed—EPA No. WS12-1 and U.S. Geological Survey No. 77 with theoretical chromium concentrations of 14.3 and 20.3 μ g/L, respectively. The total chromium observations were 15.1 and 20.6 μ g/L, respectively, while the corresponding percent recoveries were 105.6 and 101.5. The precision of the test solution preparation [Cr(III) addition] and the total chromium analyses were evaluated together by determining the total chromium in the initial and final aliquots of each of the four study test solutions. The mean (M) total chromium concentration was 0.464 mg/L with a standard deviation (s) of \pm 0.012 mg/L and a coefficient of variation (s/M) of 0.0259.

Influence of Chlorine on Chromium Speciation

The character of the chlorine-adjusted Cincinnati tap water used in preparing the four test solutions in this study is presented in Table 3. The analyses revealed that the tap water had a low alkalinity, chloride, and sulfate, and a pH above neutral. The primary and secondary inorganic constituent levels were below the maxim limits specified in the drinking water regulations.

Table 3. Characterization of Chlorine-Adjusted Cincinnati

Characteristic*	Observation
Alkalınity (as CaCOs)	36.0
Arsenic	< 0 0005
Barıum	0.25
Cadmium	< 0 002
Chloride	20 1
Chlorine, free residual	2 04
Chromium, total	< 0 005
Color, c.u.	2
Conductance, specific,	
umhos/cm at 25°C	290
Copper	< 0.02
Fluoride	0.9
Iron	< 0.1
Lead	< 0.005
Magnesium	7 1 1
Manganese	< 003
Mercury	< 0 0005
pH, units	8.05
Residue, total filterable	
(total dissolved solids)	175
Selenium	< 0.05
Silver	< 0.03
Sodium	11.
Sulfate	58 .
Turbidity, n t u	0.08
Zinc	< 0.02

^{*}Unit is mg/L unless otherwise noted.

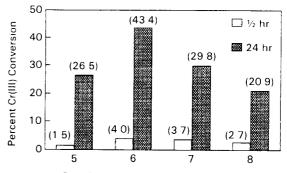
The character of the four initial and final test solutions is presented in Table 4. The analyses revealed that the 36.0 mg/L alkalinity level of the chlorine-adjusted tap water was altered by the final pH adjustment after the Cr(III) addition The alkalinity levels of the four initial test solutions with pH levels adjusted to 5, 6, 7, and 8 were 0, 13.6, 30 4, and 36.5 mg/L, respectively. During the subsequent 24-hr exposure study, these alkalinity levels were not altered significantly, however. The mean TOC level of the four initial test solutions was 1.57 \pm 0.02 mg/L; it increased slightly to 1.70 \pm 0.07 mg/L during the test. This 8-percent increase probably reflects sampling and analytical variation. The dissolved oxygen (DO) analyses were performed only on the final four test solutions because of instrumental malfunction. In each case, the observed final DO approximated the aqueous saturation level for the test temperature and pressure. Thus little, if any, oxygen consumption appears to have occurred during the test.

FRC, however, declined in each of the four test solutions during the 24-hr exposure. The concentration decreases ranged from 0.44 to 0.79 mg/L, with changes \geq 0.65 mg/L in those solutions with initial pH levels \leq 6.0

The chromium analyses revealed that the oxidation of trivalent chromium to hexavalent chromium definitely occurred in the test solutions prepared from Cincinnati tap water containing 2 04 mg/L FRC and 0.464 \pm 0.012 mg/L Cr(III) with initial pH levels of approximately 5, 6, 7, and 8. Because of the time elapsed between initiation of the test solution exposures and color development in the hexavalent chromium analyses, the initial and final hexavalent observations actually represent the 1/2- and 24-hr levels. The Cr(VI) concentrations in the four initial test solutions were all low, ranging from 0.007 to 0 019 mg/L. In the 24-hr test solutions, however, the Cr(VI) levels were more significant and ranged from 0.094 to 0 199 mg/L. The percent Cr(III) conversion to Cr(VI) appeared to vary with the initial pH of the solution (Figure 1) In the 24-hr test solutions with the initial pH levels of 6 and 8, the observed maximum and minimum conversions were 43.4 and 20 9%, respectively

Chromium oxidation by chlorine has also been observed by other investigators. In 1978, Toyama et al. (15) reported observing the formation of hexavalent chromium in solutions initially containing 10 mg/L Cr(III) and 20 mg/L

Figure 1. Percent Cr(III) conversion to Cr(VI) in Cincinnati tap water containing 0 5 mg/L Cr(III) and 2.04 mg/L FRC.



Test Solution Number (Initial solution pH)

Table 4. Periodic Characterization of Test Solutions

Test Solution No.	Sampling Period		F	Free Residual	Total		***	Total	Dissolved
	Initial	Final	pΗ	Chlorine (mg/L)	Cr (mg/L)*	Cr(VI) (mg/L)	Alkalınıty (mg CaCO₃/L)	Organic Carbon (mg/L)	Oxygen (mg/L)
5	X		4 99	2 04	0 482	0 007	0	1.56	
		X	4.15	1 25	0.476	0126	0	1.65	9. 4
6	X		6 03	2.05	0 470	0.019	136	1.61	
		X	5 95	1.40	0 459	0 199	132	1 65	9.4
7	X		6 99	2.04	0 464	0 017	30.4	1.56	
		X	6.39	1 60	0 466	0 1 3 9	29.6	1.70	96
8	X		8 04	2 04	0.447	0 012	36 5	1.54	
_		X	7.30	1 59	0.450	0 094	36.4	1.80	<i>9 5</i>

^{*}Each test solution was originally spiked with 0.5 mg/L Cr(III)

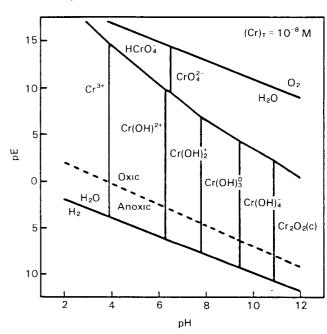
chlorine (added as sodium hypochlorite) and having pH levels ranging from <1 to 13. After 2.5 hr, the Cr(VI) levels varied from 0.1 to 1.35 mg/L, the highest level being observed in the solution with an initial pH of 7. Clifford and Chau (11) have just completed an extensive study of the fate of chromium in chlorinated water and will soon be reporting the conversion of Cr(III) and Cr(VI) in various aqueous solutions with pH levels ranging from 5 to 10.3.

Although the effects of chlorine on the speciation of chromium in aqueous solutions have been observed by several investigators, chlorine apparently has not been included as a factor in the various diagrams or models of chromium speciation. In a recent summary of the thermodynamic properties and environmental chemistry of chromium, Schmidt (16) presented a number of illustrations of the distribution of chromium species at various pH and redox potential (pE) levels. He indicated that the pE/pH diagram, reproduced here as Figure 2, predicts many, but not all, of the previously reported chromium speciation observations in natural waters. He emphasized that some of the occurrences of chromium species resulted from chromium complexation and reduction by organic matter, adsorption and oxidation by manganese oxides in suspended matter, and reduction by hydrogen sulfide (H₂S) Consequently, Schmidt introduced a modified model (Figure 3) to demonstrate the influence of these factors on chromium speciation in the environment. He further reported the incorporation of the chromium thermodynamic data into the geochemical computer model MINTEQ, currently being developed by his colleagues at Battelle Pacific Northwest Laboratory. Perhaps a model for the speciation of chromium in chlorinated drinking water could possibly be derived by incorporating the appropriate chlorine thermodynamic data into this program.

Conclusions and Recommendations

This investigation has demonstrated that trivalent chromium can be oxidized to hexavalent chromium in a tap water with a low alkalinity, chloride, sulfate, and TOC content Intest solutions with initial pH levels ranging from 5 to 8, the quantity of Cr(VI) formed from 0 464 mg/L Cr(III)

Figure 2. pE-pH diagram of aqueous inorganic Cr species at total Cr concentrations of 10⁻⁸ M (reprinted with permission, see reference 16).



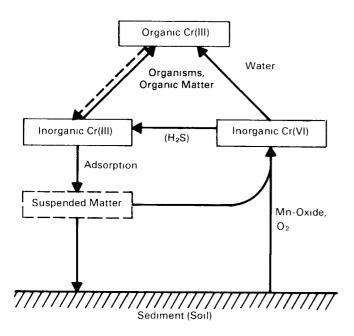
in 24 hr ranged from 0.094 to 0.199 mg/L (20.9 to 43.4 percent conversion).

Our knowledge and understanding of the conditions under which trivalent chromium oxidizes to hexavalent chromium in aqueous solutions containing free residual chlorine might be enhanced by the incorporation of appropriate chlorine thermodynamic data into the MINTEQ program and the development of a model for chromium speciation in the presence of FRC.

Acknowledgments

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Figure 3. Model of processes controlling the distribution of Cr in the environment (reprinted with permission, see references 16 and 17).



technical suggestions. The author also greatly appreciates the analytical assistance of Jim Caldwell, William Chaney, Carl Shadix, and Lou Trombly, all of the aforementioned Branch. Thanks are also expressed to Brad Smith, Organics Control Branch, for conducting the TOC determinations.

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