State of the Science of Hexavalent Chromium in Drinking Water

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INTRODUCTION

Chromium typically occurs in two oxidation states in the natural environment, water treatment processes and water distribution systems: trivalent chromium (chromium-3, Cr(III), Cr^{+3}), and hexavalent chromium (chromium-6, Cr(VI), Cr^{+6}). Trivalent chromium has been considered an essential human nutrient. Recent studies, however, have shown no deleterious effects from low Cr(III) in the diet and there is no known biological mechanistic function for Cr(III) in cells calling into questions whether Cr(III) is truly an essential nutrient (Di Bona et al. 2011). Hexavalent chromium has been demonstrated to be a human carcinogen when inhaled. The health effects of hexavalent chromium through ingestion—the dominant exposure route for drinking water—are currently under review at the federal level by the U.S. Environmental Protection Agency (USEPA).

Hexavalent chromium in drinking water was first brought to the public's attention in 1993 when Erin Brockovich highlighted contamination in groundwater near Hinkley, CA. In 2010, the Environmental Working Group (EWG) reported trace levels of hexavalent chromium in 31 of 35 US tap waters tested (Environmental Working Group, 2010); although this was not a peer-reviewed scientific study, it did renew public interest in hexavalent chromium. USEPA is currently considering whether or not to establish an MCL specifically for hexavalent chromium (USEPA, 2011a). A February 2011 U.S. congressional hearing largely focused on the EWG study (U.S. Senate Committee on Environment and Public Works 2011) further highlighted the hexavalent chromium issue. The goal of this review is to better inform potential regulatory action on this issue by summarizing what is known about hexavalent chromium, as well as pointing out gaps in current knowledge.

CHROMIUM HEALTH EFFECTS SUMMARY

This review is not intended to cover all aspects of health effects of hexavalent chromium or to critically review the decades of toxicology reports. There are a number of excellent summaries of such studies, as noted below.

Hexavalent chromium is classified as a known human carcinogen by inhalation routes of exposure (USEPA, 1998; IARC, 1990). Decades of epidemiological studies have shown that occupational exposure of workers in various industries (electroplating, chrome pigment, mining, leather tanning, and chrome alloy production) to airborne hexavalent chromium posed increased risks of lung cancer. Assessments of the carcinogenic potential of inhaled hexavalent chromium are summarized in the Integrated Risk Information System (IRIS) for chromium (USEPA, 1998), Kimbrough et al (1999), and references in IARC (1990).

In September 2010, USEPA released a draft of the Toxicological Review of Hexavalent Chromium (oral) (USEPA, 2010c) for external peer-review and public comment. Comments from both the public and peer-reviewers will be considered in finalizing this draft document. At present (May 2012) this document is still under review. Although the final toxicological report will include both noncancer and cancer effects of hexavalent chromium in drinking water, this review will focus on the cancer risks. A brief summary of the information under review regarding cancer effects is given below.

Genotoxicity. The genotoxicity of hexavalent chromium has been well described using a variety of bacterial and mammalian cell cultures and *in vivo*, as reviewed by California Office of Environmental Health Hazard Assessment (OEHHA), (2011), Thompson et al, (2011a), Zhitkovich (2011), Sedman et al, (2006), and Proctor et al, (2002). Because of its chemically similar structure, the chromate anion (CrO_4^{2-}) will enter the cell via active sulfate transporters (Collins et al, 2010). Trivalent chromium is not actively transported, but enters cells through slow diffusion. Once hexavalent chromium is absorbed into the cell, it is reduced to trivalent chromium, via low molecular weight thiols such as glutathione and cysteine and antioxidants such as ascorbate. All cell types can take up hexavalent chromium and all cell types can reduce hexavalent chromium to trivalent chromium (McCarroll et al, 2010). The intracellularly reduced trivalent chromium binds directly to DNA (Cr(III)-DNA adduct) and also causes DNA-protein cross linkages (Costa et al, 1997), leading to mutagenesis. In addition, the reduction of hexavalent chromium within the cell leads to the formation of unstable Cr(V) and Cr(IV) and thiol radicals; hexavalent chromium also reacts with oxygen to form reactive oxygen species (ROS), such as hydroxyl radicals and hydrogen peroxide radicals. The production of hexavalent chromium intermediates and ROS causes damage to DNA and mutagenesis.

Epidemiology. Unlike toxicity testing for arsenic, where millions of people worldwide have been exposed to elevated levels in arsenic in drinking water, epidemiological studies of oral exposure of humans to environmental hexavalent chromium via drinking water are limited. A highly referenced study was published by Zhang and Li (1987), where the authors concluded that deaths from all cancers, including stomach cancer, were higher in villages with elevated hexavalent chromium in the drinking water in Liaoning Province, China, than in the general population. The same authors reevaluated the data and concluded no increase cancer risks were observed (Zhang & Li, 1997); this paper however was retracted by the journal in July 2006, due to the authors' failure to disclose financial and intellectual input to the paper (Brandt-Rauf, 2006). More recent statistical analysis of the data from China showed a cancer effect (Beaumont et al, 2008). Kerger et al (2009) however concluded no significant risk of mortality from all cancers for the hexavalent chromium exposed villagers when compared with demographically similar villagers; they excluded an industrial town from the control group used by Beaumont et al (2008). Linos et al (2011) recently reported significant increases in primary liver cancer mortality in citizens exposed to hexavalent chromium in drinking water in Oinofita Greece compared with the control population. These exposures were at significantly lower concentrations (44-158 µg/L) compared with the study in China (up to 20 mg/L), yet statistically higher mortality rates from liver and lung cancers in both males and females and urologic cancer in females were observed in the exposed populations; death from stomach cancer also increased in the exposed population although the increase was not statistically significant.

There have been few other epidemiology studies reported in the literature. The limitations of these studies include small number of observed cancer cases that decrease the statistical power of the study, short follow up period that decreases the ability to detect effects that would be observed after an appropriate latency period, and lack of reporting individual exposure levels, routes of exposure, and organ specific tumors (Kerger et al, 2009; Beaumont et al, 2008; Sedman et al, 2006; Proctor et al, 2002).

Mode of Action. Because of the lack of data on carcinogenicity of hexavalent chromium to humans via oral routes of exposure from drinking water, the State of California nominated hexavalent chromium to the National Toxicology Program (NTP) (U.S. Department of Health and Human Services) for further study. The animal studies were conducted over a two-year period to determine toxicity and carcinogenicity of hexavalent chromium via ingestion in drinking water (National Toxicology Program, 2008; Stout et al, 2009). The authors concluded that hexavalent chromium, as sodium dichromate dihydrate, in drinking water caused oral cancers in rats and cancer of the small intestine in mice. Rats were exposed to 20-180 mg/L hexavalent chromium and mice to 20-90 mg/L hexavalent chromium. Statistically significant increases in cancer rates were observed only at higher doses, although trend tests were significant (Stout et al, 2009). Results from other animal studies on the toxicity of hexavalent are summarized by California OEHHA (2011), Zhitkovich (2011), Sedman et al (2006), and Proctor et al (2002). The NTP study however is the only experiment where mice and rats were exposed to hexavalent chromium in drinking water over a 2-year period.

The NTP report is being used by the EPA to evaluate carcinogenicity of hexavalent chromium to humans via drinking water. The NTP report showed carcinogenicity of hexavalent chromium to mice. Mode of action (MOA) analysis provides a description of events leading to adverse health effects in animals so that these effects can be translated to human health risks of exposure.

McCarroll et al (2010) and Thompson et al (2011a) both used the USEPA Guidelines for Carcinogen Risk Assessment (USEPA, 2005b) and the NTP data to evaluate the MOA and risk of human consumption of drinking water. Two conflicting assessments emerge as illustrated in Figure 1. With ingestion of water containing hexavalent chromium, some fraction of the hexavalent chromium will be reduced to non-toxic trivalent chromium in saliva and in the acid environment of the stomach. These protective processes have been described to be overwhelmed only by high chromium dosing (De Flora, 2000), such as used in the NTP study (Thompson et al, 2011a). Sedman et al (2006) however stated that their review of the literature showed that hexavalent chromium was not completely converted to trivalent chromium in animal or human stomachs; 10-20% of ingested low dose hexavalent chromium would not be reduced in the GI system of humans (Zhitkovich, 2011). Stern (2010) and Collins et al (2010) using data from the NTP study, concluded that the carcinogenicity of hexavalent chromium did not result from saturating the reducing capacity of the mouse GI tract. Stern's analysis of the data showed that the reduction capacity of the mouse GI tract was not exceeded even at the highest dosing of hexavalent chromium in the drinking water, yet some amount of hexavalent chromium was still absorbed, leading to formation of tumors in the small intestines.

Once absorbed, hexavalent chromium is reduced to trivalent chromium with formation of Cr-DNA adducts and other DNA damage resulting in mutagenesis, cell proliferation and tumor formation in the GI tract (MOA I in Figure 1) (California OEHHA, 2011; Zhitkovich, 2011; McCarroll et al, 2010). Thompson et al (2011a) however described the MOA as reduction of hexavalent chromium resulting in oxidative stress, due to production of Cr(V), Cr(IV), and ROS, as described above, inflammation, cell proliferation, direct or indirect damage to DNA, and mutation (MOA II in Figure 1).

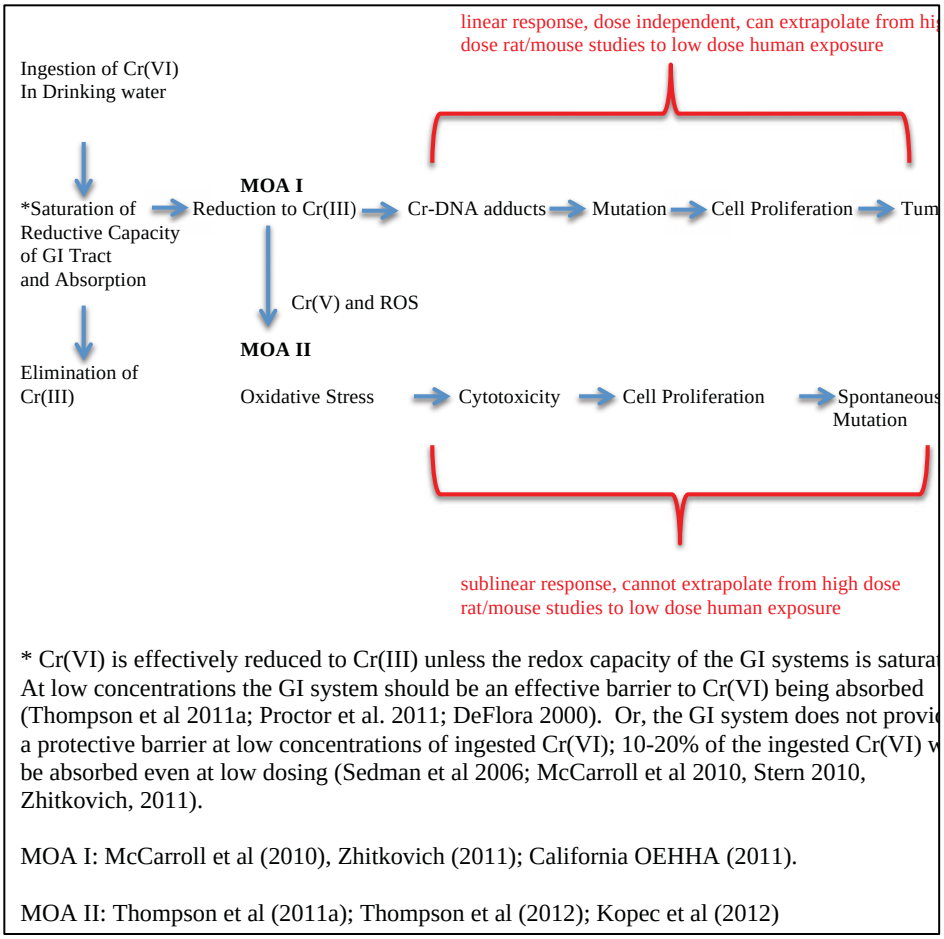

Figure 1: Proposed mode of action for cancer effects in humans from ingestion of hexavalent chromium in drinking water

Linear extrapolation of cancer risk data to low environmental doses is the default regulatory approach for carcinogens with a mutagenic MOA. Data, as evaluated by McCarroll et al (2010), Stern (2010), and supported in reviews by Zhitkovich (2011) and California OEHHA (2011), show a mutagenic MOA supporting use of linear extrapolation for the oral risk assessment. Thompson et al (2011a) and Proctor et al (2011) argue for a nonlinear MOA and thus a nonlinear low-dose response; a linear extrapolation from higher dosing studies would overestimate health effects at low dosing.

Recently Thompson and co authors conducted a 90 day exposure of mice to hexavalent chromium in drinking water at doses ranging from 0.3 to 520 mg/L (Thompson et al, 2011b) and 0.1 to 180 mg/L hexavalent chromium (Kopec et al, 2012; Thompson et al, 2012). There was a dose dependent decrease in the ratio of reduced to oxidized glutathione in the duodenum of mice indicating oxidative stress, whereas levels of 8-hydroxydeoxyguanosine, a measure of oxidative DNA damage, were not altered (Thompson et al, 2011b; Thompson et al, 2012). Gene expression was examined in GI tissue of these mice using a genome-wide microarray analysis (Kopec et al, 2012). Hexavalent chromium caused gene expression changes associated with oxidative stress again supporting the MOA II proposed by Thompson et al (2011a). There is continued scientific debate regarding the MOA of hexavalent chromium with discussion of the two proposed MOAs.

The references above provide technical discussion of the MOAs regarding criticisms of methods employed and data interpretation.

In February 2012, the EPA announced a delay in finalizing the IRIS assessment so that the recently published research by Thompson, Kopec, and co-workers, as referenced above, and other studies would be included. EPA anticipates that the draft assessment for hexavalent chromium will be released for public comment and external peer review in 2013 with final assessment by Fall 2014 (USEPA, 2012b).

REGULATIONS

The United States Environmental Protection Agency (USEPA) has regulated total chromium (trivalent chromium plus hexavalent chromium) under the National Primary Drinking Water Regulations (CFR Section 40 Part 141) since 1992. The non-enforceable maximum contaminant level goal (MCLG), established solely on the basis of protecting consumers against potential health problems, is 100 μg/L (0.1 mg/L). The maximum contaminant level (MCL) is the enforceable standard that must be met by drinking water systems, and is set as close to the MCLG as feasible. EPA must consider the costs and benefits when developing the MCL. The MCL for total chromium equals the MCLG at 100 μg/L, with the listed potential health effect of allergic dermatitis (USEPA, 2010a). In March 2010, USEPA reviewed the chromium regulation as part of the second Six Year Review (USEPA, 2010e). On May 2, 2012, USEPA announced that utilities will be required to monitor for Cr(VI) under the Third Unregulated Contaminant Monitoring Rule (UCMR3) (USEPA, 2012a). As explained in the previous section, in September 2010, USEPA released a draft toxicological review of hexavalent chromium human health effects (USEPA, 2010d). The peer review panel workshop on the draft assessment was held on May 12, 2011 (USEPA, 2010c), and EPA released the comments from the public comment period and peer review workshop in July 2011. Once the health assessment is finalized USEPA will determine if a new MCL should be set specifically for hexavalent chromium, or if a revision of the current MCL for total chromium is warranted.

The State of California established its own total chromium MCL of 50 μg/L (0.05 mg/L) in 1977 (California Department of Public Health, 2012). A non-enforceable Public Health Goal (PHG) for hexavalent chromium of 0.02 μg/L (20 ppt) was issued in July 2011 (California OEHHA, 2011), and California will now proceed with setting an MCL for hexavalent chromium. As with a federal standard, the State will set the MCL as close to the PHG as is economically and technically feasible. The State of New Jersey has also considered whether to propose a state MCL for hexavalent chromium, with a health-based MCL estimated at 0.07 μg/L (70 ppt) (New Jersey Drinking Water Quality Institute, 2010).

The World Health Organization (WHO) *Guidelines for Drinking-water Quality* state, "...because the health effects are determined largely by the oxidation state, different guideline values for chromium(III) and chromium(VI) should be derived. However, current analytical methods and the variable speciation of chromium in water favour a guideline value for total chromium." Accordingly, WHO set the provisional guideline value for total chromium in drinking water at 50 μg/L, pending additional data and review (World Health Organization, 2003). It is important to note that this guideline was set in 2003, prior to the publication of the NTP and other recent health effects studies.

CHROMIUM ANALYSIS

Analytical terminology. Before discussing the various techniques for chromium analysis, several terms related to analytical capabilities must be defined.

> The method detection limit (MDL), as defined by the EPA (USEPA, 1986), is the lowest concentration of an analyte reportable with 99% confidence that the value is greater than zero. It is determined by analyzing seven replicates of a standard solution with a concentration of hexavalent chromium near the estimated detection limit and multiplying the standard deviation (SD) by the Student's t value for degrees of freedom (n-1) of 6 and (α-1) = 0.99 (MDL = SD*3.143 for n = 7).
>
> The Lowest Concentration Minimum Reporting Limit (LCMRL) is defined as "the lowest *spiking* concentration such that the probability of spike recovery in the 50% to 150% range is at least 99%". Details of the method used to determine the LCMRL are given by USEPA (2010f). The LCMRL will be greater than the MDL.
>
> The Minimum Reporting Level (MRL) is the minimum concentration that can be reported by a laboratory as a quantified value (USEPA, 2010b).

The MDL is referenced by many older methods and data falling below the MDL were often censored or reported as "below detection limit." USEPA is now moving towards using the LCMRL and MRL to determine if data meet quality control criteria.

Total chromium analysis. There are many analytical methods for determining low-μg/L levels of total chromium (trivalent chromium plus hexavalent chromium); those approved for monitoring drinking water under the Safe Drinking Water Act (40 CFR Part 141 §141.23) are listed in Table 1. Prior to analysis, total chromium samples are collected in plastic or glass bottles and preserved with HNO_3, and have a 6 month holding time (Electronic Code of Federal Regulations, 2011b).

However, recent work has shown that there can be significant problems with the determination of chromium in real water samples by these methods. For example, MWH Laboratories conducted a study in which more than 1500 drinking water samples were analyzed for both hexavalent chromium and total chromium (Eaton et al, 2001). This study found that for nearly half of the 770 samples with significant (> 1 μg/L) chromium, hexavalent chromium concentrations measured by Ion Chromatography (IC) were greater than the total chromium concentration indicated by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Obviously, a sample cannot contain more than 100% hexavalent chromium, leading the authors to propose several reasons why the ICP-MS method may not be accurately quantifying the total chromium in the sample, including a difference in behavior of trivalent chromium versus hexavalent chromium within the ICP-MS or a problem with sample preservation (Eaton et al, 2001).

Table 1 Approved methods for measuring total chromium in drinking water

Method	Technique	Method Detection Limit (µg/L)	Reference
EPA 200.5 (Rev 4.2)	Axially viewed inductively coupled plasma - atomic emission spectrometry	0.2 (MRL = 0.5)	USEPA, 2003
EPA 200.7 (Rev 4.4)	Inductively coupled plasma - atomic emission spectrometry	4	USEPA, 1994a
EPA 200.8 (Rev 5.4)	Inductively coupled plasma – mass spectrometry	0.08	USEPA, 1994b
EPA 200.9 (Rev 2.2)	Stabilized Temperature Graphite Furnace Atomic Absorption	0.1	USEPA, 1994c
Standard Methods 3113B	Electrothermal Atomic Absorption Spectrometry	2	APHA et al, 2005 or equivalent online (APHA et al, 2011)
Standard Methods 3120 B	Inductively coupled plasma emission spectroscopy	7	APHA et al, 2005 or equivalent online (APHA et al, 2011)

Total chromium analysis is also complicated by the presence of iron. A study of both synthetic and real drinking waters found that samples containing even low levels of particulate iron can sorb chromium, and that this "particulate chromium" is often lost from solution and not measured, even in acidified samples (Parks et al, 2004). Chromium can also occur as "fixed chromium" associated with solids (often iron oxides) that are not dissolved by an acid digestion, requiring hydroxylamine or microwave-assisted acid digestion for full recovery (Kumar & Riyazuddin, 2009; Parks et al, 2004; Parks & Edwards, 2002). USEPA guidance for "total recoverable analyte" analysis under the third Unregulated Contaminant Monitoring Regulation (UCMR3) now requires that all samples be acid digested, regardless of sample turbidity (USEPA, 2010g).

Hexavalent chromium analysis by Ion Chromatography (IC). Hexavalent chromium reacts with 1,5-diphenylcarbazide in acid solution forming a pink complex of unknown composition (Method 3500-Cr D) (APHA et al, 2005). This procedure has been used for decades for hexavalent chromium analysis using a spectrometer set at 540 nm with a molar absorptivity of 40 000 $g^{-1}cm^{-1}$ (Rowland, 1939) and a working range of 100 to 1000 µg/L (APHA et al, 2005). Reported interferences for this colorimetric method are molybdenum, vanadium and mercury, but only at high concentrations (APHA et al, 2005).

This colorimetric method was combined with ion chromatography (IC) in EPA Method 218.6 (USEPA, 1994d), in order to separate hexavalent chromium from the sample matrix to minimize interferences, and concentrate the hexavalent chromium, thus improving the detection limit. Method 218.6 is titled "Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater, and Industrial Wastewater Effluents by Ion Chromatography" and thus was not specifically developed for drinking water analyses. In this method, filtered (0.45 µm) water samples are adjusted using a concentrated ammonium sulfate/ammonium hydroxide buffer (2500

mM ammonium sulfate and 1000 mM ammonium hydroxide). The buffer is added drop wise into the filtered sample to a pH of 9-9.5. At this pH hexavalent chromium exists as chromate, CrO_4^{2-}, that is separated from other anionic species present in the sample on an analytical column (Dionex IonPac AS7 or equivalent). Diphenylcarbazide is added using a post column mixing coil and the complex formed is measured at 530 nm using a flow-through spectrometer. The MDL for this method is listed as 0.3 µg/L in drinking water and ground water (USEPA, 1994d), and the MRL is 0.4 µg/L (Eaton, 2011).

Method 218.6 was adapted in 2003 (Dionex, 2003; Thomas et al, 2002) to improve the detection limit. Improvements to the method included: lowering the flow rates for the eluent (1 ml/min) and the post column reagent (0.33 ml/min), a larger injection volume (1 ml), and a larger reaction coil (750 µl). The modified method also uses 10 times less ammonium sulfate (250 mM) in the sample-adjusting buffer. Injecting 1 ml of sample, instead of the 50-250 µL sample specified in Method 218.6, with the original buffer may overload the analytical column due to the high concentration of ammonium sulfate. The MDL with these modifications is reported as 0.018 µg/L. Further modifications were published in 2011 (Dionex, 2011) to achieve a MDL of 0.001 µg/L. These improvements included further decreases to the eluent flow rate (0.36 ml/min) and post column flow rate (0.12 ml/min) and the use of a 2 mm guard and analytical column instead of 4 mm columns. The Lowest Concentration Minimum Reporting Limit (LCMRL) for this method, using a simulated drinking water matrix, is reported as 0.019 µg/L (USEPA, 2010f).

None of the methods for hexavalent chromium is approved for compliance with the Safe Drinking Water Act (SDWA), since, at present, hexavalent chromium is not a regulated chemical under the SDWA. In anticipation of the inclusion of hexavalent chromium in the third round of the Unregulated Contaminant Monitoring Rule (UCMR3) and the possible promulgation of a hexavalent chromium MCL, the USEPA has released a method to update Method 218.6. This method, Method 218.7 "Determination of Hexavalent Chromium in Drinking Water by Ion Chromatography with Post-Column Derivatization and UV–Visible Spectroscopic Detection," was developed specifically for drinking water, and to meet expected requirements for lower detection of hexavalent chromium. The method describes two IC systems for analysis, each using different eluents (ammonium sulfate/ammonium hydroxide versus sodium carbonate/sodium bicarbonate), column and reaction coil sizes, and flow rates. All other components of the analysis are the same as in Method 218.6. The MDL ranges from 0.0044 to 0.015 µg/L and the LCMRL from 0.012 to 0.036 µg/L, depending on the type of preservative (solid or liquid) and eluent system used (USEPA, 2011c). This new method is sufficient for detecting hexavalent chromium concentrations at the California PHG of 0.02 µg/L.

Listed interferences in Method 218.6 and 218.7 are contamination, matrix interferences, and oxidation-reduction reactions of chromium (USEPA, 2011c; USEPA, 1994d). Contamination is associated with reagents or glassware. All glassware should be cleaned with 50% nitric acid or 1 part nitric acid + 2 parts hydrochloric acid + 9 parts water. Reagent blanks must be monitored for detection of contamination. Because of the physical separation of hexavalent chromium from other anions on the IC column and the specificity of the complex formation of hexavalent chromium with diphenylcarbazide, chemical interferences are not expected. High ionic strength may affect response; however, hexavalent chromium recoveries were greater than 80% in testing with 1000 mg/L chloride and 2000 mg/L sulfate (Dionex, 2003). Use of laboratory fortified samples allows determination of matrix effects.

As with any redox sensitive chemical in water samples, the preservation of the oxidation state of chromium at time of collection is critical. The presence of oxidizing or reducing agents, either natural or added for drinking water treatment, may alter the oxidation state of chromium in the collected sample. pH also plays a major role in the redox chemistry of chromium. The addition of a buffer to raise the pH of the sample to pH 9-9.5 is required in Method 218.6 (USEPA, 1994d) and all subsequent modifications of this procedure. A liquid ammonium buffer consisting of 250 mM ammonium sulfate and 1000 mM ammonium hydroxide is added to the sample to adjust the pH. Method 218.6 specified using 2500 mM ammonium sulfate, but later methods use a lower concentration of the salt (250 mM) to minimize overloading of the analytical column. At pH 9, the oxidizing potential of hexavalent chromium is too low to react with any reductant that may be present in the sample (Kotas & Stasicka, 2000). Method 218.6 recommends that the buffer be added dropwise to pH 9-9.5 using a pH meter to ensure each sample's pH is properly adjusted. However, in Method 218.7, the recommended adjustment is to pH > 8, using 1 mL of the buffer added to a 100 ml sample, with confirmation of the pH > 8 required upon sample receipt at the laboratory. Method 218.7 also allows for the use of a solid buffer consisting of 13.3 mg Na_2CO_3, 10.5 mg $NaHCO_3$ and 33 mg $(NH_4)_2SO_4$ per 100 mL sample (nominally 1.25 mM Na_2CO_3, 1.25 mM $NaHCO_3$ and 2.5 mM $(NH_4)_2SO_4$). The use of ammonium in both the liquid and solid buffers is to remove the oxidizing potential of chlorine by forming chloramines. There is ongoing research on the effectiveness of preservation buffers under various environmental conditions and water chemistries by the EPA and others. The California Department of Public Health (California Department of Public Health, 2011) has also proposed a buffer for use in source water sampling, using borate and sodium carbonate with potassium bicarbonate to avoid the use of ammonium-based buffers.

The original EPA method (Method 218.6) required samples to be filtered through a 0.45 µm filter prior to preservation. The IC manufacturer initially recommended not filtering samples before preservation, but rather filtering them just prior to injection into the IC (Dionex, 2003). Current manufacturer guidance (Dionex, 2011), California Department of Health guidelines, and EPA Method 218.7 do not require field filtration of samples or filtration before injection.

With respect to holding time, EPA Method 218.6 allows preserved samples to be held for only 24 hours, while water sampling under 40 CFR 136 allows a holding time of 28 days for preserved samples (Electronic Code of Federal Regulations, 2011a). With a recent review of the literature, the EPA is now allowing a holding time of 5 days (USEPA, 2011b) for voluntary hexavalent chromium monitoring, while Method 218.7 lists a holding time of 14 days.

Hexavalent chromium analysis by HPLC – ICPMS. There are numerous other methods for speciating chromium including various precipitation steps and solid or liquid phase extractions, followed by spectroscopic analysis (Pyrzynska, 2011; Gomez & Callao, 2006; Kotas & Stasicka, 2000; Marqués et al, 2000). For example, many researchers have utilized high-performance liquid chromatography (HPLC) coupled with inductively coupled plasma mass spectrometry (ICP-MS) to conduct a speciation analysis for chromium (Table 2). Soluble trivalent chromium typically exists as Cr^{3+}, $CrOH^{2+}$, or $Cr(OH)_2^+$ in natural waters while hexavalent chromium exists as $HCrO_4^-$ or CrO_4^{2-}. Since the trivalent chromium species are all positively charged ions and the hexavalent chromium species are negatively charged ions, they can be separated using either anion or cation exchange. After this separation, ICP-MS can be used to quantify the concentration of each chromium species.

Table 2 Select list of past studies detailing chromium speciation by HPLC-ICPMS

Column	Eluent	Parameters	Method Detection Limit (µg/L)		Reference
			Cr(VI)	Cr(III)	
Excelpak ICS-A23 (anion)	1 mM EDTA-2NH_4 + 0.01 M oxalic acid	Injection volume 0.5 mL; pH 7; peaks separated within 480 s	0.088	0.081	Inoue et al, 1995
Dionex IonPac AS7 (anion)	EDTA to complex Cr(III), then 35 mM ammonium sulfate + ammonium hydroxide	Injection volume 0.1 mL; pH 9.2; peaks separated within 720 s	1.0	0.4	Byrdy et al, 1995
Cetac ANX1606-Cr (anion)	0.25% nitric acid	Injection volume 0.01 mL; separated within 500 s	0.18	0.06	Powell et al, 1995a
Dionex IonPac AG5 (anion)	Discontinuous - Step 1: 0.3 M nitric acid, Step 2: 1 M nitric acid	Injection volume 0.1 mL; separated within 420 s	0.2	0.1	Barnowski et al, 1997
Shodex RSpak NN-814-4DP (multi-mode)	90 mM ammonium sulfate + 10 mM ammonium nitrate	Injection volume 0.025 mL; pH 3.5; separated within 480 s	0.5	0.5	Hagendorfer & Goessler, 2008
Dionex CG5A (anion + cation groups)	Discontinuous – Step 1: 0.35 M nitric acid Step 2: 1 M nitric acid	Separated within 500 s	0.19	0.32	Seby et al, 2003
Hamilton PRP-X100 (anion)	Discontinuous – 20 mM ammonium nitrate + 60 mM ammonium nitrate (due to As speciation)	Injection volume 0.1 mL; pH 8.7; sample time 600 s	0.13	n/a	Martinez-Bravo et al, 2001
Dionex IonPac AS7 (anion)	EDTA to complex Cr(III), then 50 mM ammonium nitrate	Injection volume 1 mL; pH 8; separated within 700 s	0.012	0.005	Gurleyuk & Wallschlager, 2001
Hypersil GOLD	2 mM EDTA + 0.25 mM tetrabutylammonium phosphate (TBAP)	Injection volume 0.2 mL; pH 6.9; separated within 260 s	0.009	0.017	McSheehy & Nash, 2006
Brownlee C8	2 mM tetrabutyl-ammonium hydroxide (TBAOH) + 0.5 mM K_2EDTA + 5% methanol	Injection volume 0.05 mL; pH 7.6; separated within 100 s	0.1	0.1	Wolf et al, 2011

Both the HPLC and the ICP-MS components must be optimized to achieve low detection limits. HPLC must achieve a good separation between peaks for trivalent and hexavalent chromium with a high signal-to-noise ratio. Depending on the type of column used, HPLC may only quantify one of the chromium species. For example, a cation-exchange column can be used to capture Cr(III) so that only the Cr(VI) is left to be analyzed by ICP-MS. In this case, the Cr(III) can only be quantified by measuring total chromium by ICP-MS and calculating the difference. Parameters that must be optimized when using HPLC include column type, eluent composition and pH, and injection volume. Of these, the choice of eluent may be the most important. Acidic eluents may reduce Cr(VI) to Cr(III). EDTA has been used to complex Cr(III) into an anion, although EDTA cannot completely preserve Cr(III) in chlorinated samples (Alan Zaffiro, Shaw Environmental, Personal Communication, October 11, 2011).

The ICP-MS analysis typically looks at the two most abundant masses of chromium: ^{52}Cr and ^{53}Cr at 83.8% and 9.6%, respectively. A drawback of using ICP-MS is the formation of polyatomic interferences on these two isotopes when carbon or chlorine is present (e.g. $^{40}Ar^{12}C$, $^{35}Cl^{16}O^{1}H$, and $^{37}Cl^{16}O$). This means that waters with high alkalinity or salt content will result in more background noise and therefore higher detection limits. These polyatomic interferences can also result if an organic eluent is used for the HPLC separation. Some ICP-MS instruments can be operated in “reaction cell” or “collision cell” mode, wherein argon plasma gas is supplemented with helium or some other gas (typically hydrogen or ammonia), resulting in a lower background and better limit of detection due to a reduction in argon-containing polyatomic species. However, it is important to note that currently Method 200.8 (Table 1) does not allow for the use of this technology in ICP-MS analysis, so chromium measurements must be corrected by subtracting concentrations of polyatomic interferences or samples must be digested to remove the carbon (USEPA, 1994b). As mentioned previously, the UCMR3 guidelines require all samples to be digested using a modified nitric acid digestion, regardless of sample turbidity (USEPA, 2010g).

Field Speciation Method for Hexavalent Chromium. Another method for determining hexavalent chromium is based on a field method using a cation exchange column (Ball & McCleskey, 2003). The general idea is that passing water through this column will remove trivalent chromium (a cation) but not hexavalent chromium (an anion). This method has a reported detection limit of 0.05 μg/L for hexavalent chromium when coupled with graphite furnace atomic absorption spectrometry (GFAAS); however, rigorous testing of artifacts in the presence of constituents such as Natural Organic Matter (NOM) has not been conducted. Previous work suggests that NOM can bind trivalent chromium, converting it into an anion that can pass through the column and give a "false positive" of hexavalent chromium in samples (Icopini & Long, 2002). Additional research is needed to confirm and quantify this potential limitation. Another limitation to this method is the inability to determine breakthrough, or the ‘false positive’ that could result if samples were high in ionic strength or high in trivalent chromium. Finally, the presence of iron, and especially particulate iron, can result in lower recovery of chromium due to sorption or co-precipitation (Parks et al, 2004). Ball and McClesky (2003) confirmed this lower recovery of chromium during their method development at levels of iron above 1 mg/L; however they attributed it to the reduction of Cr(VI) to Cr(III) caused by the oxidation of Fe(II) to Fe(III). More work is needed to confirm the role of iron when concentrations above 1 mg/L are present.

CHROMIUM CHEMISTRY IN WATER TREATMENT AND DISTRIBUTION

Forms of chromium and trends in sorption and solubility. Chromium has two main oxidation states: trivalent chromium (Cr(III), chromium-3, Cr^{+3}), and hexavalent chromium (Cr(VI), chromium-6, Cr^{+6}). The pE-pH diagram describes the relative importance of Cr(III) and Cr(VI) at equilibrium and the dominant species (Figure 2). As a general rule, Cr(VI) is expected to predominate in highly oxygenated drinking water or when strong oxidants such as chlorine or even moderately strong oxidants like chloramine are present in water. At low Cr concentrations in typical drinking water conditions (Figure 2), Cr(VI) is present as monovalent $HCrO_4^-$ below pH 6.5 and divalent CrO_4^{2-} between pH 6.5 to 10 (Rai et al, 1987; Butler, 1967; Tong & King, 1953). At very low or no oxygen levels, Cr(III) is the dominant species, which will be in cationic (Cr^{+3}, $CrOH^{+2}$, or $Cr(OH)_2^+$) or neutral ($Cr(OH)_3^0$) form depending on the pH (Rai et al, 1987; Hem, 1977). Cr(III) tends to be extremely insoluble (< 20 μg/L) between pH 7 and pH 10, with minimum solubility at pH 8 of about 1 μg/L (Rai et al, 1987).

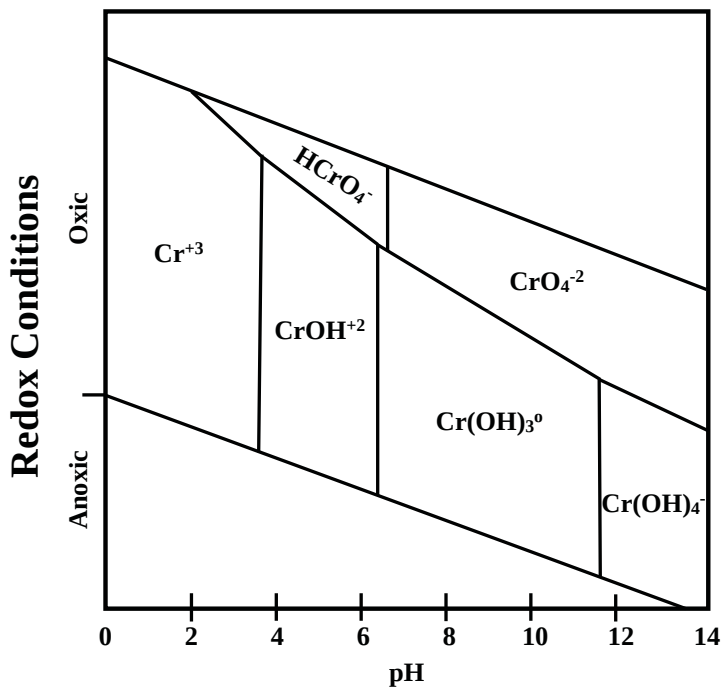

Figure 2. Speciation diagram for aqueous chromium

From a practical perspective, Cr(III) is not a health concern at levels encountered in potable water. In a given water sample, Cr(III) can be present in five forms (Figure 3): 1) as soluble Cr(III) species, 2) as a precipitated $Cr(OH)_3$ solid, 3) sorbed to the surface of $Fe(OH)_3$ and other oxides, 4) "fixed" inside oxides in a form that is relatively inaccessible from solution, and 5) complexed with naturally occurring organic matter such as humic and fulvic acids (Icopini & Long, 2002). Although Cr(VI) can undergo similar reactions, it is much more likely to remain soluble. These different types of chromium are key to understanding issues of importance in analytical chemistry, water treatment and distribution.

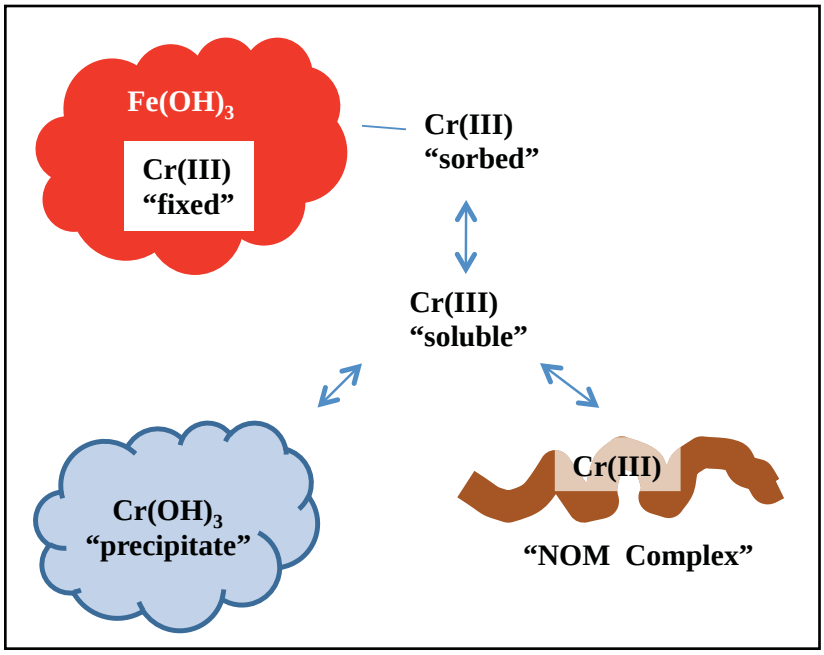

Figure 3. Dissolved or soluble Cr(III) in water can sorb to oxide surfaces, complex with natural organic matter, form precipitated solids such as $Cr(OH)_3$, or be trapped in solids relatively inaccessible from the water as "fixed" Cr(III).

The relative importance of each type of Cr(III) will vary dramatically. Depending on circumstances, including level of organic matter, $Fe(OH)_3$ and other oxides, pH, and other factors, the soluble fraction of Cr(III) can range from 0-100%. To illustrate, predictions are made for a sample with 2 mg/L ferric iron particulates (4 mg/L as $Fe(OH)_3$) containing either 5 µg/L Cr(III) or 5 µg/L Cr(VI) using the model of Dzombak and Morel (1990). If the iron hydroxide does not dissolve, the models predict that Cr(III) will be virtually 100% sorbed over the range from pH 6 to 11 (Figure 4).

In contrast, Cr(VI) will be virtually 100% soluble above pH 8.0, while from pH 2-6 less than 10% of Cr(VI) is soluble (Figure 4). Sorption of Cr(VI) to iron oxides or hydroxides starts to become highly significant (> 50%) below about pH 7. Cr(VI) also forms no significant precipitates at levels encountered in potable water and does not strongly bind to natural organic matter. Hence, Cr(VI) is generally present in drinking water as a soluble anion, and its potential human toxicity is a much greater concern than Cr(III).

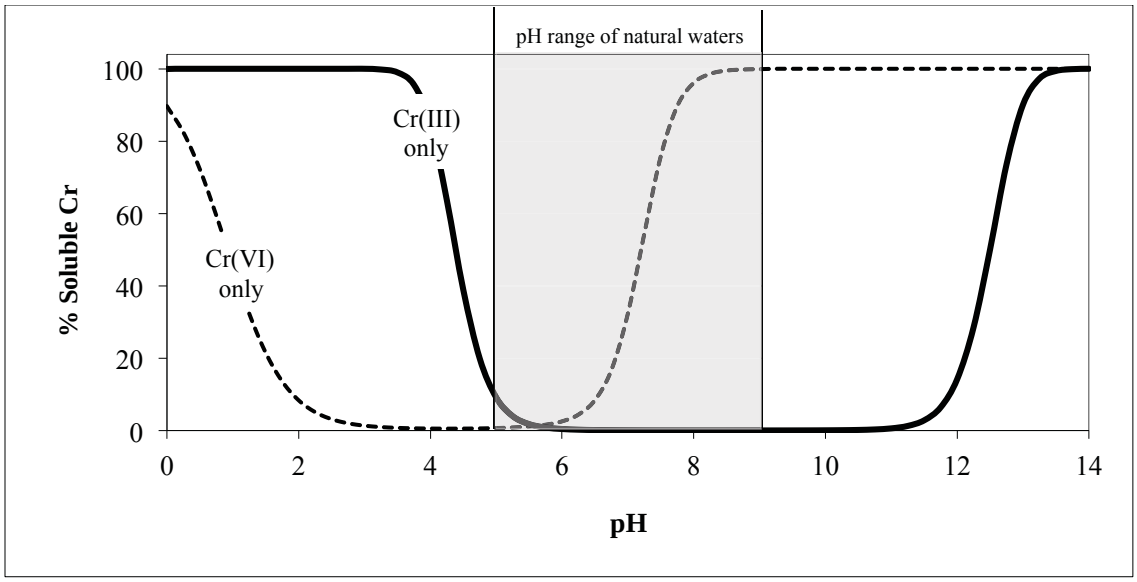

Figure 4. Model prediction of soluble Cr(III) and Cr(VI) in a drinking water sample in the presence of iron particles. Conditions: Cr(III) or Cr(VI) = 5 μg/L, Fe = 2 mg/L (4 mg/L $Fe(OH)_3$), I = 0.01 M, using diffuse layer model of Dzombak and Morel (1990).

Overview of reactions of engineering importance. In drinking water collection, treatment, and distribution systems, virtually all transformations from Cr(III) to Cr(VI), and vice versa, are mediated by constituents that are either naturally present in or purposefully added to water (Table 3). Due to rapid changes that are possible in dissolved oxygen, chlorine, chloramine, pH, and Fe(II), it is frequently the case that waters are not at equilibrium. In such cases the kinetics of the transformations between Cr(VI) and Cr(III) become very important.

Table 3 General Reactions of Cr(III) and Cr(VI) in Water Treatment and Distribution

Description	Occurs in the Presence of...	Typical Location
Cr(III) Oxidation to Cr(VI)		
Fast (minutes to hours)	MnO_2 solids $2Cr^{3+}+3MnO_2+2H_2O = 2CrO_4^{2-}+3Mn^{2+}+4H^+$ Chlorine, H_2O_2, $KMnO_4$ $2Cr^{3+}+3HOCl+5H_2O = 2CrO_4^{2-}+3Cl^-+13H^+$ $2Cr^{3+}+3H_2O_2+2H_2O = 2CrO_4^{2-}+10H^+$ $5Cr^{3+}+3MnO_4^-+8H_2O = 5CrO_4^{2-}+3Mn^{2+}+16H^+$	Oxygenated high pH groundwater, water treatment, distribution system
Slower (hours to days)	Chloramine $2Cr^{3+}+3NH_2Cl+8H_2O = 2CrO_4^{2-}+3NH_3+3Cl^-+13H^+$	Distribution system
Slowest (days to years)	Dissolved Oxygen $4Cr^{3+}+3O_2+10H_2O = 4CrO_4^{2-}+20H^+$	Groundwater, distribution system

Description	Occurs in the Presence of...	Typical Location
Cr(VI) Reduction to Cr(III)		
Fast (minutes to hours)	Fe^{+2}, Stannous chloride, sulfites $CrO_4^{2-}+3Fe^{2+}+8H^+ = Cr^{3+}+3Fe^{3+}+4H_2O$ $2CrO_4^{2-}+3Sn^{2+}+16H^+ = 2Cr^{3+}+3Sn^{4+}+8H_2O$ $2CrO_4^{2-}+3SO_3^{2-}+10H^+ = 2Cr^{3+}+3SO_4^{2-}+5H_2O$	Lower DO groundwater, water treatment, distribution system
Slower (days to years)	Absence of dissolved oxygen, sulfides, numerous bacteria $2CrO_4^{2-}+3S^{2-}+16H^+ = 2Cr^{3+}+3S^o+8H_2O$	Groundwater, potentially in iron mains/dead ends
Conversion of Soluble Cr to Particulate Cr		
Fast (seconds to hours)	Water pH > 5.0	Possible whenever soluble Cr(III) is above ≈ 1 μg/L
	Fe or Al oxides	Addition of coagulant

The first reaction of interest is the oxidation of non-toxic Cr(III) to more toxic Cr(VI) (Table 3). To the extent this reaction occurs over a period of years or even geologic timespans in oxygenated groundwater, "naturally occurring" Cr(VI) can be present in the influent to potable water treatment plants and distribution systems at relatively high levels (see following section). More rapid conversion of Cr(III) to Cr(VI) can occur in the presence of added oxidants (Table 3), which is of concern because even if Cr(VI) is completely removed at treatment plants, it could potentially reform in the distribution system at significant levels when these oxidants contact soluble Cr(III) or plumbing surfaces that contain chromium. These oxidation reactions also complicate analysis of many compliance or monitoring samples, because much higher levels of Cr(VI) can be detected than were originally present when samples were collected.

The role of oxygen in the oxidation/reduction of chromium is deserving of additional research. For example, it is predicted that the oxidation of Cr(III) to Cr(VI) is thermodynamically favored in the presence of detectable oxygen. However, studies attempting to confirm this reaction at pH 4.0, 5.9, 8.6, and 9.9 quantified conversion of Cr(III) to Cr(VI) of only 3% after 50 days (Eary & Rai, 1987; Schroeder & Lee, 1975). The transformation might be more significant at warmer temperatures found in household water heaters. Schroeder and Lee (1975) found the conversion rate of Cr(III) to Cr(VI) to be three times faster at 45°C than at room temperature (22 - 26°C), although they only tested that temperature for one week. Conversely, Izbicki et al (2008) found that reduction of Cr(VI) to Cr(III) occurred when oxygen levels fell below 0.5 mg/L, even though the reaction is not thermodynamically favored in water with no oxygen.

Cr(III) can be oxidized to Cr(VI) by free chlorine (Saputro et al, 2011; Lai & McNeill, 2006; Brandhuber et al, 2004; Bartlett, 1997; Clifford & Chau, 1988; Ulmer, 1986; Sorg, 1979), and there is one report that chloramine can oxidize Cr(III) to Cr(VI) over a period of hours to days (Brandhuber et al., 2004). Potassium permanganate (Lai & McNeill, 2006; Brandhuber et al, 2004) and manganese oxides (Nico & Zasoski, 2000; Zhang, 2000; Fendorf et al, 1992; Fendorf & Zasoski, 1992; Eary & Rai, 1987) also mediate this reaction. Hydrogen peroxide will oxidize trivalent chromium (Rock et al, 2001; Rock, 1999) although in very acidic solutions hydrogen peroxide actually acts as a catalyst for the reduction of Cr(VI) to Cr(III) (Pettine et al, 2002).

Reactions that reduce Cr(VI) to Cr(III) are also important (Table 3). In fact, this reduction is the first step in many effective water treatment strategies, followed by conversion of the soluble Cr(III) to particulate $Cr(OH)_3$ or sorbed solids that can be settled or filtered from the water. The most common reductant is ferrous iron (Fe(II)), with reaction times on the order of seconds to hours, depending on pH (Blute, 2010; McGuire et al, 2006; Qin et al, 2005; Lee & Hering, 2003; Schlautman & Han, 2001; Buerge & Hug, 1999; El-Shoubary et al, 1998; Pettine et al, 1998b; Buerge & Hug, 1997; Sedlak & Chan, 1997; Fendorf & Li, 1996; Henderson, 1994; Lin et al, 1992; Eary & Rai, 1988; Philipot et al, 1984). The presence of dissolved oxygen does not significantly interfere with reduction of Cr(VI) by Fe(II) (Schlautman & Han, 2001; Eary & Rai, 1988). Zero-valent iron (Fe^0) can also be oxidized to produce Fe(II), which will in turn reduce Cr(VI); iron electrodes and permeable subsurface barriers containing iron filings or shavings have been successfully used to reduce high levels of Cr(VI) in industrially-contaminated groundwaters (Døssing et al, 2011; Liu et al, 2008; He et al, 2004; Alowitz & Scherer, 2002; Mayer et al, 2001; Astrup et al, 2000; Ponder et al, 2000; Yang & Kravets, 2000; Blowes et al, 1997; Pratt et al, 1997; Powell et al, 1995b; Brewster & Passmore, 1994; Gould, 1982). Other iron solids present in water distribution pipes, such as hematite, magnetite, ilmenite and green rusts can also serve as a source of ferrous iron for Cr(VI) reduction (Loyaux-Lawniczak et al, 2000; Kiyak et al, 1999; Khaodhiar, 1997; Peterson et al, 1997a; Peterson et al, 1997b; Peterson, 1996; White & Peterson, 1996; Eary & Rai, 1989; Anderson et al, 1984).

Cr(VI) can also be reduced by many reduced sulfur compounds including thiols (Szulczewski et al, 2001), iron sulfide (Kim et al, 2001; Patterson et al, 1997; Zouboulis et al, 1995), metabisulfite (Patterson et al, 1994), sodium sulfide and sodium sulfite (Lai & McNeill, 2006; Brandhuber et al, 2004), and hydrogen sulfide (Kim et al, 2001; Pettine et al, 1998a), as well as stannous chloride (Lai & McNeill, 2006; Brandhuber et al, 2004), ascorbic acid (Xu et al, 2004), and a variety of organic compounds (Buerge & Hug, 1998; Hug et al, 1997; Deng & Stone, 1996; Wittbrodt & Palmer, 1996; Wittbrodt & Palmer, 1995; Popov et al, 1992; James & Bartlett, 1983; Bartlett & Kimble, 1976; Schroeder & Lee, 1975). Cr(VI) can also be reduced under aerobic and anaerobic conditions by microbes; this can involve direct reduction by chromium reducing bacteria as well as indirect reduction via production of hydrogen sulfide or ferrous iron by sulfate-reducing and iron-reducing bacteria, respectively (Boni & Sbaffoni, 2009; Somasundaram et al, 2009; Vainshtein et al, 2003; Gandhi et al, 2002; Wielinga et al, 2001; Chen & Hao, 1998).

CHROMIUM OCCURRENCE

Chromium is the 21st most abundant element in the earth's crust (Nriagu & Nieboer, 1988). Chromium can be introduced into aqueous solution either by natural weathering of chromite ore ($FeO{\bullet}Cr_2O_3$) and other chromium-bearing minerals, or by contamination from a variety of industrial sources including processes using chromium for metal alloys, metal plating, wood treatment, leather tanning, and corrosion control (Kimbrough et al, 1999). Kharkar et al (1968) reported an average total chromium value in river water of 1.4 μg/L, while Richard and Bourg (1991) report total dissolved chromium concentrations from zero to 208 μg/L for unpolluted waters, with typical values given of 0.5 μg/L for rivers and 1.0 μg/L for groundwaters.

Naturally occurring hexavalent chromium. While it is often the case that Cr(VI) in drinking water is evidence of anthropogenic contamination, over the last decade there have been many reports of naturally occurring Cr(VI) in groundwater and at very high levels (Table 4).

Table 4 Reports of naturally occurring hexavalent chromium

Location	Hexavalent chromium (µg/L)	Description	Reference
Cazadero County, CA	12 - 22	Spring water from ultramafic rock	Oze et al, 2004
La Spezia, Italy	5 - 73	Groundwater from ophiolite complex	Fantoni et al, 2002
Leon Valley, Mexico	12	Groundwater from ultramafic rock	Robles-Camacho & Armienta, 2000
Mojave Desert, CA	60	Groundwater from mafic alluvial deposits	Izbicki et al, 2008; Ball & Izbicki, 2004
Santa Cruz County, CA	4 - 33	Groundwater from Aromas Red Sands aquifer, residing within ophiolite complex	Gonzalez et al, 2005
New Caledonia	700	Pore-water from phosphorus-amended soil derived from ultramafic rock	Becquer et al, 2003
Idaho National Laboratory, ID	1.9 – 7.7	Groundwater sampled upstream of contamination site	Raddatz et al, 2011
Paradise Valley, AZ	up to 220	High pH and oxygenated groundwater, no dissolved iron or organic matter	Robertson, 1975
Urania, Sao Paulo, Brazil	up to 120; mean from 144 wells = 45	High concentrations of Cr in aquifer sandstones and pyroxenes	Bourotte et al, 2009
Yilgarn Craton, Australia	10 - 430	Ground water from fresh and weathered ultramafic rocks	Gray, 2003
Sacramento Valley, CA	Up to 70	Aquifer in Quaternary alluvium with outcrops of ultramafic rocks	Dawson et al, 2008
San Francisco, CA	Up to 98	Serpentine bedrock	Henrie et al, 2004

Since the vast majority of chromium found in natural minerals is Cr(III), there has been considerable effort to define natural mechanisms by which Cr(III) may be oxidized to Cr(VI). As discussed above, Cr(III) can be oxidized to Cr(VI) in the presence of manganese oxides, specifically pyroluscite (β-MnO_2) (Eary & Rai, 1987). They believed that manganese oxides and

oxygen were the only naturally occurring compounds capable of transforming Cr(III) to Cr(VI). Their studies over a broad range of pH (3 – 10.1) with and without aeration, demonstrated that the reaction was not a function of oxygen concentration and that the reaction was very slow in slightly acidic to basic solutions (limited by the low solubility of $Cr(OH)_{3(s)}$). They also theorized that the kinetics of chromium oxidation in soil from minerals such as birnessite (γ-MnO_2) or cryptomalene (α-MnO_2) would be even faster. Recent follow-up investigations (Oze et al, 2007) confirmed that birnessite can convert Cr(III) to Cr(VI) at a rate between 0.5 and 4.1 nM/hr (0.026 – 0.213 μg/L/hr) and that the oxidation of Cr(III) by Mn-oxides is inhibited at pH > 4 due to the precipitation of $Cr(OH)_3$ on the MnO_2 surface (Fendorf et al, 1992). Another study found that native MnO_2 could oxidize Cr(III) to Cr(VI), yielding as much as 100 μg/L Cr(VI) leaching from sediments (Chung et al, 2001). Johnson and Xyla (1991) show that Cr(III) is oxidized to Cr(VI) on the surface of manganite but that the reaction is not pH dependent. They tested a pH range of 3.5 – 9.5 and concluded that there is a critical adsorption density above which the reaction is inhibited.

Chromium occurrence in drinking water. The full extent of chromium occurrence in US drinking water sources is not known, and the available data must be carefully viewed in light of the difficulties of low-level analysis. A 1962 USGS study of the 100 largest US drinking water supplies found a median total chromium concentration of 0.43 μg/L with a range of non-detect to 35 μg/L (Durfor & Becker, 1962). A similar study in Canada found a median total chromium concentration of 2 μg/L for raw, treated, and distributed water, with a range of ≤ 2 to 14 μg/L (Meranger et al, 1979). Richard and Bourg (1991) report an average total dissolved chromium concentration of 0.4 μg/L for tap waters. Chromium concentrations were measured during the 1996 National Arsenic Occurrence Survey of 514 drinking water sources throughout the U.S. (Chen et al, 1999; Edwards et al, 1998); however, since the survey sample design focused on arsenic, the local chromium data cannot be extrapolated to predict national occurrence of chromium. Nevertheless, the data provide insight on typical levels occurring in drinking water sources; total chromium concentrations ranged from zero to 76 μg/L, with an average concentration of 3.5 μg/L. Most recently, in 2010 USEPA published results from the "Six Year Review 2" of regulated contaminant occurrence in public drinking water supplies. For the nearly 186,000 records analyzed, 15.3% of samples had detectable total chromium, with a median detectable concentration of 4.2 μg/L, and 90th percentile detectable concentration of 10 μg/L (USEPA, 2010b). These represent a lower bound on the occurrence of chromium because in many cases the reporting limit was at 10 μg/L, resulting in artificial censoring of the data. An ongoing research project funded by the Water Research Foundation (Project 4414) is further evaluating these data in light of varying detection and reporting limits.

Data on Cr(VI) in drinking water are even more scarce. This is primarily because Cr(VI) is not regulated in drinking water and accurate speciation methods for measuring low–μg/L levels of Cr(VI) have only recently been developed (Dionex, 2011; USEPA, 2011c; Dionex, 2003; Thomas et al, 2002). The State of California Department of Health Services instituted a Cr(VI) sampling program for California water utilities from 1997-2009, and found that approximately one-third of the ~7000 sources sampled had Cr(VI) at or above the 1 μg/L detection limit, with 4.5% of the sources above 10 μg/L (California Department of Public Health, 2011). A Water Research Foundation (WaterRF) project in 2004 surveyed more than 400 drinking water sources (before treatment) across the U.S. and found an average Cr(VI)

concentration of 1.1 μg/L, with the median concentration below the detection limit of 0.2 μg/L (Frey et al, 2004). More recently, the Environmental Working Group (EWG) issued a non-peer-reviewed report showing Cr(VI) occurrence ranging from non-detect to 12 μg/L in tap waters of 35 U.S. cities (Environmental Working Group, 2010). Although the methodology of this report could not be confirmed, the results were widely reported in the popular media and spurred renewed public interest in hexavalent chromium.

ENGINEERING CONSIDERATIONS FOR CHROMIUM TREATMENT

Reducing consumer exposure to elevated levels of Cr(VI) in potable water at reasonable cost requires a sound understanding of: 1) origins of the Cr(VI) at consumers' taps, 2) systematic evaluation of possible control points and removal technologies, and 3) cost/benefit and feasibility analysis for the particular situation (Figure 5).

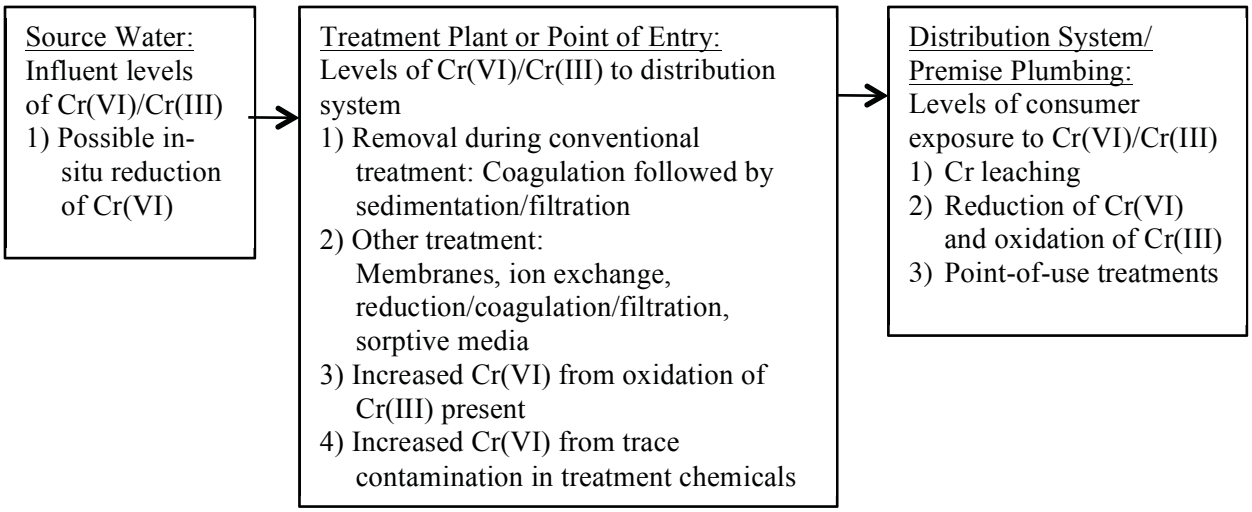

Figure 5. Overview of potential engineering controls for Cr(VI) in potable water treatment and distribution.

Origins of the hexavalent chromium at the tap. It is generally assumed that Cr(VI) levels at the point of entry to the distribution system reflect those observed at the consumer's tap. However, only very preliminary work has been conducted to confirm these beliefs, and several studies actually show the opposite. One study in Chicago, IL in the 1960's found that 17% of water samples had "pickup" of chromium, meaning that tap water samples had more Cr than water leaving the treatment plant (Craun & McCabe, 1975). Frey et al (2004) collected "profiles" of Cr(VI) in raw water, through treatment plants, and in distribution systems for more than one dozen systems. While in many cases only small changes in Cr(VI) levels were observed, in one system Cr(VI) in the distributed water increased by about 10 μg/L (1.3 to 11.9 μg/L) and in another system Cr(VI) decreased by about 20 μg/L (from 22.2 down to 0.4 μg/L). Although only a single profile was collected in each system and results are confounded by influence of multiple source waters, the results do warrant additional research.

Cr(VI) at the consumer's tap may arise from a variety of sources. As discussed previously, source waters may have naturally-occurring or anthropogenically elevated levels of Cr(VI) in the source water. Chromium may also be a trace contaminant in treatment chemicals. For example, Eyring et al (2002) measured chromium in alum coagulants, potentially yielding 0.24 μg/L chromium in water at commonly applied alum doses. More recently, a water treatment plant in Missouri found that Cr(VI) increased from 0.1 μg/L in the raw water to 0.6 μg/L at the end of the treatment plant (Missouri Department of Natural Resources, 2010), with the suspected source being the plant's alum and/or lime. Chromium may be added to water via leaching from distribution system materials or through reactions with main distribution system or premise plumbing. Chromium is contained in materials typically used in water plant and distribution system infrastructure such as cast iron (Burgess & Briggs, 1956), cement (Kayhanian et al, 2009; Hills & Johansen, 2007; Guo et al, 1998; Bobrowski et al, 1997; Guo, 1997; Webster & Loehr, 1996), and stainless steel (Tuthill, 1994; Geld & McCaul, 1975), and this chromium could be released to the water through leaching or corrosion of these materials. In this case, mitigation strategies would need to consider approaches similar to those used for lead and copper corrosion control.

It is not known if the chromium that is added or leached would be Cr(III) or Cr(VI), but as discussed above, any Cr(III) could be oxidized to Cr(VI) by added oxidants (such as potassium permanganate) and disinfectants (chlorine, chloramine) used in the treatment plant. These reactions may occur even in the timeframe of "hours" that water is retained in treatment plants (Lai & McNeill, 2006; Brandhuber et al, 2004), raising the prospect that Cr(VI) may have characteristics of a disinfection by-product due to its formation over much longer times in water distribution systems. In contrast, systems with unlined iron pipes may sometimes function effectively as passive "zero valent iron" Cr(VI) treatment systems, due to release of Fe(II) to water from pipe corrosion and resulting rapid reduction of Cr(VI) to Cr(III). However, it would be important to avoid mobilizing any particulate chromium that is precipitated in this manner (Lytle et al, 2010; Reiber & Dostal, 2000). Much more research is needed to systematically evaluate the relative importance of these issues if it is desired to reduce consumer exposure at the tap.

Hexavalent chromium removal strategies. There are numerous potential control points at which Cr(VI) could be effectively removed to reduce consumer exposure, including: 1) in-situ source water treatment to remove Cr(VI) from the influent water, 2) engineered treatment processes to remove Cr(III) and Cr(VI), 3) operation and maintainance of the water distribution system including secondary disinfectant residual type and dose, and 4) point of use devices (Table 5). Ultimately, the effectiveness of each strategy and relative cost/benefits will be dependent on the source water chemistry, pre-existing treatment processes and facilities, chromium concentrations, water scarcity, residuals handling concerns, and the origins of the Cr(VI) as indicated in Figure 5 and prior discussion. The ultimate point of compliance for any Cr(VI) MCL (i.e., at the entry point to the distribution system vs. within the distribution network or at the tap) will also influence the treatment strategies. For example, if Cr(VI) at the tap was due to oxidation of Cr(III) in the distribution system, a treatment process to remove Cr(III) would have to be implemented.

Table 5 Summary of Key Issues Related to Engineering Controls

Technique/Issue	Level of Understanding for Low Level Cr(VI)	Key Limitation or Concern	Illustrative References
Cr(VI) Removal Techniques			
In-situ removal from source water	Relatively few examples/studies for potable water	Removal of Fe(II) or reduced sulfur compounds and Cr(III) at treatment plant, cost effectiveness uncertain.	USEPA, 2005; Fruchter, 2002; Mayer et al, 2001
Cr removal during conventional coagulation treatment (co-precipitation with $Al(OH)_3$ or $Fe(OH)_3$)	Some	Ferric and alum coagulants have limited effectiveness for Cr(VI); concerns about oxidation of Cr(III) during backwash water recycling	Sharma et al, 2008
Cr(VI) reduction without removal of particulates	High. Potentially very low cost	Reoxidation of Cr(III) to Cr(VI), residual Fe(II) or stannous compounds in distributed water.	Brandhuber et al, 2004; Eary & Rai, 1988
Cr(VI) reduction and filtration	High	Cost associated with retrofit for Fe(II) and potential expense of new treatment plant.	Blute & Wu, 2012; Qin et al, 2005; Hering & Harmon, 2004; Lee & Hering, 2003; Clifford et al, 1986
Membranes (removal as Cr(VI))	High	Overall cost, and expense/treatment of reject water.	Yoon et al, 2009; Yoon et al, 2002; Drago, 2001; Faust & Aly, 1998
Weak Base Anion (WBA) exchange	Moderate	pH adjustment needed, disposal of spent resin	Blute & Wu, 2012; Blute et al, 2010; Blute et al, 2007; McGuire et al, 2006
Strong Base Anion (SBA) Exchange	Moderate	Regeneration and brine disposal	Blute & Wu, 2012; Blute et al, 2010; Blute et al, 2007; McGuire et al, 2006
Sorption	Not demonstrated	Poor selectivity, poor performance at pH 7-9, and issues/expense/effectiveness of regeneration.	McGuire, 2010; McGuire et al, 2006; Mohan & Pittman Jr, 2006; Edwards & Benjamin, 1989
Point of Use	High	Maintenance and affordability.	Drago, 2001
Cr(VI) Formation Concerns			
Cr(III) oxidation via disinfection	Virtually no occurrence data.	Even if Cr(VI) is removed or neglible in source water, can form during disinfection and distribution.	Lai & McNeill, 2006; Lee & Hering, 2005; Brandhuber et al, 2004; Frey et al, 2004

Technique/Issue	Level of Understanding for Low Level Cr(VI)	Key Limitation or Concern	Illustrative References
Cr(VI) leaching from cement, cast iron, or stainless steel	Virtually no information in drinking water.	Not reported although Cr(VI) can be present.	See previous discussion in text
Possible Cr(VI) formation in water heater	Virtually no information.	Higher temperatures and pHs reportedly favor Cr(VI) formation.	Schroeder & Lee, 1975
Passive Cr(VI) Reduction			
Reduction from bacteria, Fe(II) from iron mains	Virtually no data.	May reduce human exposure versus Cr(VI) levels in treatment plant.	See previous discussion in text

There has been considerable success applying "in situ" treatments to remove Cr(VI) in groundwater via injection of reducing agents to the aquifer, even in waters contaminated at the mg/L level (Table 5). The general idea is that the added Fe(II) salts or reduced sulfur species, in conjunction with detention times on the order of days to years, can completely convert Cr(VI) to Cr(III) (i.e., (Fruchter, 2002)). However, it is important to note that all other oxidants must also be scavenged by the Fe(II) to assure that the Cr(III) is not re-oxidized, and excess Fe(II) must also be controlled to avoid subsequent precipitation in finished water. With levels of Cr(VI) over 100 μg/L, removal of the newly formed Cr(III) during subsequent treatment will also be of concern.

A comprehensive review of Cr(VI) removal via engineered treatment processes was recently conducted (Sharma et al, 2008), and some comprehensive evaluations of viable treatment processes and cost evaluations have also been completed for Cr(VI) removal at California utilites (Blute & Wu, 2012; Blute et al, 2010; Blute, 2010; McGuire, 2010; McGuire et al, 2007; McGuire et al, 2006; Qin et al, 2005; Lee & Hering, 2003; Drago, 2001). These have confirmed that treatment via reductive coagulation can easily obtain very low levels (< 5 μg/L) of Cr(VI) in water leaving the treatment plant. Other techniques including membranes, weak base anion (WBA) exchange and strong base anion (SBA) exchange are also effective, with some performance sensitivities related to water chemistry, and at relatively higher cost, residual handling, and water losses (McGuire et al, 2006; Drago, 2001). WBA treatment consists of polymeric resin that must be utilized at pH 6 for effective Cr(VI) removal so pH readjustment is often necessary. SBA resin is also able to remove Cr(VI) from water but requires significant amounts of salt for regeneration and requires brine disposal. Reductive coagulation with filtration (RCF) is more labor intensive than either WBA or SBA exchange due to mulitiple treatment steps and aeration or pH adjustment may be required depending on influent water chemistry. In addition, wastes from these processes can be classified as hazardous, such that special procedures may be necessary for disposal (Blute & Wu, 2012). There is limited work showing that Cr(III) can be removed during conventional alum or ferric coagulation via co-precipitation with $Al(OH)_3$ or $Fe(OH)_3$, but this is not effective for removing Cr(VI) (Sharma et al, 2008). Sorptive media are promising but to date, have never acheived the selectivity or capacity necessary to be reliable or cost effective (Sharma et al, 2008; McGuire et al, 2006; Edwards & Benjamin, 1989).

At the tap, point-of-use treatments such as reverse osmosis and anion exchange can remove Cr(VI) (Drago, 2001), and are also potentially attractive due to the fact that only the small volumes of water used for cooking or drinking must be treated. Treating only the water that is consumed yields major benefits in terms of longer run lengths for a given volume of media in the case of ion exchange, and a lesser volume of wasted water for reverse osmosis. On the other hand, these home units must be maintained and used properly to be effective.

RECOMMENDATIONS FOR FURTHER WORK

The future impact of hexavalent chromium on the drinking water community is uncertain. Depending on the outcome of the health effects review, USEPA may decide to promulgate an MCL specifically for hexavalent chromium, and the level at which the MCL is set will determine the magnitude of its effect. In California, where an MCL is certain, the remaining question is where that MCL will be set.

While much is known about hexavalent chromium in drinking water, this review has highlighted the following gaps in our current knowledge:

1. Uncertainty remains about the health effects of hexavalent chromium in drinking water, and there is ongoing research to examine the mode of action.
2. The newest low-level detection method for hexavalent chromium (EPA Method 218.7) should be used for sample analysis, although possible interferences from particulate forms of chromium must be investigated. Other speciation techniques (e.g. field methods, HPLC-ICP-MS or IC-ICP-MS) should also be investigated.
3. The analytical methods for measuring total chromium need to be improved, so that detection limits are comparable to methods for hexavalent chromium.
4. The extent of low levels of chromium (both total and hexavalent) in source waters and treated drinking waters needs to be identified.
5. The extent of inadvertent addition of chromium from treatment chemicals or infrastructure in treatment plants and water distribution systems should be quantified.
6. Treatment methods for removing chromium may need to be refined to meet a low MCL, and cost estimates updated to reflect any treatment modifications. Additional water qualities must be tested to evaluate the impact on cost and efficiency.
7. The issue of oxidation of Cr(III) in treated water must be addressed, so that consumers are not exposed to more Cr(VI) than expected due to speciation changes in the distribution system.

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