

Chromium in Drinking Water: A Technical Information Primer

Objective

This technical information primer is intended to inform drinking water systems about chromium in drinking water and identifies resources and references that systems may find helpful in addressing chromium-related concerns. The following sections provide background and general information, as well as specific information regarding occurrence, health effects, regulatory aspects, analytical methods, and treatment technologies. Systems may choose to use select information from this document and the referenced materials to craft a utility-specific document.

Background

Chromium is a metallic element found in rocks, soils, plants, and animals. It is used in steel making, metal plating, leather tanning, corrosion inhibitors, paints, dyes, and wood preservatives. The most common forms of chromium in the environment are trivalent, hexavalent and the metal form.

The USEPA regulates total chromium in drinking water and has set a Maximum Contaminant Level (MCL) of 0.1 mg/L. The World Health Organization (WHO) guideline is 0.05 mg/L for total chromium. Currently, there are no federal regulations for individual chromium species in drinking water. However, in December 2010, the USEPA Administrator, Ms. Lisa Jackson announced a series of actions that USEPA will take to address hexavalent chromium in drinking water including: 1) providing guidance to water systems in sampling and monitoring, 2) finalizing a risk assessment study, and 3) determining if a federal regulation needs to be set on hexavalent chromium in drinking water (USEPA 2010). May 2, 2012 [USEPA required](#) all systems serving more than 10,000 people and a statistical sample of smaller systems to monitor for total chromium and hexavalent chromium.

General Information

What are the different terminologies used to refer to chromium?

Total chromium refers to all chromium compounds present in water regardless of oxidation state.

Trivalent chromium refers to compounds where chromium is present in +3 oxidation state.

Hexavalent chromium refers to compounds where chromium is present in +6 oxidation state.

Hexavalent chromium is commonly referred to as: chromium 6, chromium VI, chrome 6, Cr(VI), Cr+6, or hex chrome. Hexavalent chromium is also popularly known as the “Erin Brockovich chemical” after the famous case in Hinkley, CA in 1993, where hexavalent chromium contamination of groundwater resulting from industrial discharges led to the largest settlement in a direct action lawsuit in U.S. history.

What are the different forms of chromium in the environment?

The most common forms of chromium in the environment are trivalent, hexavalent, and the metal (zero valent) form. Trivalent chromium (as oxide) is the most stable form of chromium in solids, occurs naturally in many vegetables, fruits, meats, grains, and yeast, and is considered an essential

nutrient. Hexavalent chromium and chromium in the metal form are generally produced by industrial processes.

Hexavalent chromium also occurs naturally. Trivalent chromium can be oxidized to hexavalent chromium during water disinfection. Hexavalent chromium compounds are more water soluble than trivalent chromium compounds.

What are the sources of hexavalent chromium in drinking water and where is it found?

The major source of hexavalent chromium in drinking water is oxidation of naturally occurring chromium present in igneous geologic formations. There are locations where chromium compounds have been released to the environment via leakage, poor storage, or improper industrial disposal practices. Chromium compounds both trivalent and hexavalent chromium, are very persistent in water (USEPA 2011).

Occurrence Information

How abundant is chromium in the environment?

Chromium is the 21st most abundant element in the Earth's crust. Chromium is found naturally in rocks, plants, soil and volcanic dust, humans and animals. Hexavalent chromium is widely found in waters, including source waters for drinking water, at concentrations varying from sub- $\mu\text{g/L}$ levels to more than 100 $\mu\text{g/L}$.

Where in the United States does hexavalent chromium occur in water?

Hexavalent chromium can naturally occur in waters throughout the United States and can also be found in areas with anthropogenic inputs. Several occurrence studies have been performed in the United States and worldwide on the occurrence of chromium in the past 50 years. In 1962, USGS performed a survey of contaminants in the treated drinking water of the 100 largest cities of the United States (Durfor 1962), which included total chromium ranging from non-detect to 35 $\mu\text{g/L}$. However, at that time, the occurrence data were limited by the analytical capabilities in detecting low levels of chromium.

Since then multiple studies have been conducted on chromium occurrence in the environment, in the United States and other parts of the world. A Water Research Foundation (WaterRF) funded study (Frey 2004) investigated occurrence of chromium (both individual species and total) in 407 source waters of the U.S. The study found that total chromium occurs both in surface and groundwaters; however, hexavalent chromium was not found in surface waters to the same degree as in groundwaters. Total chromium in surface waters, with a few exceptions, was primarily composed of trivalent chromium. A significant fraction of groundwater results showed that the total chromium concentrations were composed exclusively of hexavalent chromium.

The California Department of Public Health maintains a database of chromium monitoring results collected by California systems, which is updated regularly (CDPH 2013). This database shows that hexavalent chromium has been detected in 2,310 drinking water sources in California.

In May 2012 USEPA finalized the [third Unregulated Contaminant Monitoring Rule](#) (UCMR3) which requires water systems serving greater than 10,000 persons and a subset of smaller systems to

monitor for hexavalent chromium and total chromium. UCMR3 is expected to provide a more complete understanding of chromium occurrence nationally.

What fraction of total chromium in my water can be in hexavalent form?

Theoretically, up to 100% of total chromium can be present in hexavalent chromium form. However, the actual fraction of hexavalent chromium varies depending on the water type (ground water versus surface water, raw water versus treated drinking water, etc.), geographical location and the oxidation reduction potential of the water.

In the WaterRF funded study (Frey 2004), hexavalent chromium was found primarily in groundwater, and to a lesser extent in surface water, even though total chromium was found in both source waters. A significant fraction of groundwater sources showed total chromium present exclusively as hexavalent chromium.

What is the range of concentrations of chromium found in source waters?

In the WaterRF funded study (Frey 2004), in a survey of 407 source waters, total chromium was found in both groundwater and surface waters. The range of concentrations of total chromium varied from non-detect (below the method detection level at the time of 0.2 µg/L) to 47.1 µg/L. The average and median concentrations were 2 µg/L and 0.8 µg/L, respectively.

A second WaterRF funded study (Seidel et al 2012) evaluated water system compliance monitoring data collected between 1998 and 2005. While method sensitivity changed over that time (reporting levels ranged from 0.02 – 100 µg/L) this data set included 162,823 sample results. Eighty-four percent of the samples were non-detects, with over half (57%) of the non-detect values having a reporting level at 10 µg/L or higher (15% of the non-detect observations occurred when the reporting level was 5 µg/L).

This study also looked specifically at data collected in California. While the California data overlaps with the national total chromium dataset, it includes both source and finished water hexavalent chromium values. It also tends to reflect data gathered with more sensitive methods than the national compliance data as a whole. The WaterRF report is based on the California dataset as of November, 2011. At that time, large numbers of samples did not contain total chromium or hexavalent chromium above reporting limits (83% and 41% respectively).

The UCMR3 national monitoring program is ongoing (2013 – 2015) and will fill in the information gap around low-level chromium and hexavalent chromium occurrence. While available data illustrates that only 5 – 8% of water systems are likely to have total chromium at levels of 10 µg/L or higher, it is not possible to predict with confidence how many water systems have chromium at levels at or below 5 µg/L.

Health Effects Information

How are people exposed to hexavalent chromium?

Hexavalent chromium exposure can occur through people breathing it, ingesting it in food or water, or through direct contact with the skin.

Occupational exposure can occur when people work in industries that process or use chromium, chromium compounds, or chromium processes such as chromate containing pigments, spray paints, coatings, chrome plating baths, metal cutting or welding, etc.

What are the health effects of trivalent and hexavalent chromium in drinking water?

Chromium III is an essential nutrient in humans and is often added to vitamins in dietary supplement. It has relatively low toxicity and would be a concern in drinking water only at very high levels.

Chromium VI is recognized as a human carcinogen via inhalation. Inhalation of hexavalent chromium compounds increases the risk of lung cancer. Exposure to hexavalent chromium from breathing dust or fumes is considered to have a much higher risk than exposure from drinking water (OEHHA, 2010).

Research performed by the National Toxicology Program (NTP) has shown that the hexavalent chromium containing chemical sodium dichromate dihydrate causes cancer in laboratory animals following oral ingestion at high doses (NTP, 2008). Male and female rats had a significant increase of malignant tumors in their oral cavity. Studies in mice found increases in benign and malignant tumors in the small intestine, which increased with doses in both male and female mice. However, it is to be noted that the lowest doses of hexavalent chromium where carcinogenic effects were observed in these animal studies were orders of magnitude higher than humans could encounter in drinking water obtained from the most highly contaminated source waters identified in the United States (NTP, 2008).

California Environmental Protection Agency's Office of Environmental Health Hazard Assessment (OEHHA) analyzed data collected from China (Beaumont et al., 2008) that found increased rates of stomach cancer in people who were probably exposed to very high levels of hexavalent chromium in drinking water (OEHHA, 2010). Research by Dr. Silvio De Flora (De Flora, 2009), which included *ex-vivo* studies in both human and animal models indicated that hexavalent chromium genotoxicity and potential carcinogenicity tend to be attenuated or suppressed in the body. Dr. De Flora's research demonstrated efficient detoxication by reduction of hexavalent chromium to trivalent chromium or "sequestration" by saliva, gastric juice, and intestinal bacteria. Such mechanisms would limit the toxicity of hexavalent chromium after oral ingestion.

In September, 2010, USEPA released a draft human health assessment proposing to classify hexavalent chromium as likely to be carcinogenic via ingestion (USEPA 2010). USEPA was advised by a peer review panel in 2012 to consider the results from research funded through the American Chemistry Council. The new research replicates the earlier NTP study at lower doses of hexavalent chromium and seeks to identify the underlying cause for carcinogenicity from oral exposure. The completion of the USEPA human health risk assessment and final determination of human carcinogenicity of hexavalent chromium via oral ingestion is still pending.

In July, 2011 California finalized its [Public Health Goal](#) at 0.02 µg/L in drinking water. California found sufficient evidence that hexavalent chromium is carcinogenic by oral exposure, based on the NTP long-long term animal study. California also identified a health-protective level of 2 µg/L for non-carcinogenic effects based on liver toxicity in rats (NTP, 2008). The California PHG is based solely on health effects and is set at a level determined to not pose any significant risk to health.

What are the safe levels of hexavalent chromium in drinking water?

The standard (MCL) for total chromium was set in 1992 and is based on allergic dermatitis (skin reactions). The MCL was based on the protective level indicated by the science at the time. The current federal maximum contaminant level for total chromium is 0.1 mg/L.

EPA is now reviewing data from a 2008 National Toxicology Program long-term animal study and other available research, which suggests that hexavalent chromium may be a human carcinogen if ingested. When the review is complete, EPA will consider this and other information to determine whether the drinking water standard for total chromium is sufficiently protective or whether it needs to be updated.

Regulatory Information

What is the current drinking water regulatory standard for chromium?

The current federal maximum contaminant level (MCL) for total chromium is 0.1 mg/L. The current California MCL for total chromium is set at 0.05 mg/L. There are currently no federal standards for hexavalent chromium – it is covered under the total chromium MCL.

If routine monitoring indicates that total chromium levels are above the MCL, water systems must take steps to reduce the total chromium below that level. Also, water systems must notify their customers as soon as practical, but no later than 30 days after the system learns of a violation (USEPA 2011).

Is the USEPA considering new regulations for chromium?

The USEPA is currently reviewing the health effects of hexavalent chromium following the release of a long-term animal toxicity study by the National Toxicology Program in 2008. In September 2010, EPA released a draft of its assessment for public comment and external peer review (USEPA 2010). When this human health assessment is complete EPA will carefully review the conclusions and consider all relevant information to determine if a new standard needs to be set.

While USEPA is preparing its assessment of the health risk posed by hexavalent chromium, the Agency has directed water systems to collect data on hexavalent and total chromium occurrence in finished water and water in the distribution system. Data collection through the [third Unregulated Contaminant Monitoring Rule](#) began in January 2013 and will continue through 2015.

What is the difference between the Federal Maximum Contaminant Level Goal (MCLG) and California Public Health Goal (PHG) for chromium?

Under the Safe Drinking Water Act the MCLG is defined to be a non-enforceable concentration of a drinking water contaminant, set at the level at which no known or anticipated adverse effects on human health occur and which allows an adequate safety margin. The enforceable standard, maximum contaminant levels (MCLs), are set as close to MCLGs as feasible using available treatment technology and taking cost into consideration. The current MCLG and MCL for total chromium in water are both set to 0.1 mg/L.

Public Health Goals (PHGs) are set in California by the California Office of Environmental Health Hazard Assessment (OEHHA) which is part of the California Environmental Protection Agency (CalEPA).

2011). Similar to MCLGs, the PHGs are non-enforceable and are not required to be met by any public water system. They are set as goals based solely on public health risk considerations and they include a margin of safety.

MCLGs and PHGs are different in how levels for carcinogens are set. The federal MCLGs for carcinogens are set at zero, because the USEPA concluded that as a matter of policy it would not establish an ideal goal that involved a hypothetical risk. Conversely, PHGs are set at a level considered to pose no significant risk of cancer.

The PHG for hexavalent chromium in California is 0.02 µg/L, which is the estimated “one in a million” lifetime cancer risk level. This means that for every million people who drink two liters of water with that level of hexavalent chromium daily for 70 years, no more than one person would be expected to develop cancer from exposure to hexavalent chromium.

Analytical Methods Information

What analytical methods can be used for the measurement of chromium?

Total chromium concentrations of 0.2 µg/L can be reliably reported by the Inductively Coupled Plasma Mass Spectroscopy methods ([EPA 200.8 Rev 5.4](#); [USEPA 1994](#), [Standard Methods 3125 \(1997\)](#), [ASTM D5673-10](#)) when samples are digested before analysis. Graphite Furnace Atomic Absorbance can reach comparable quantification levels (e.g., [Standard Method 3113\(1999\)](#), [EPA 200.9 Rev 2.2](#); USEPA 1994). In the third Unregulated Contaminant Monitoring Rule USEPA requires use of ICP/MS methods with digestion.

Hexavalent chromium can be measured at levels as low as 0.02 µg/L by ion chromatography using a modified version of EPA Method 218.6 or EPA [Method 218.7](#), which was developed to support monitoring under the UCMR3 (EPA, 2011).

There are other research methods available for measuring hexavalent or total chromium at low levels, but they are not currently approved for compliance monitoring (Wolf 2007; McNeill 2012).

What levels of chromium can I detect using currently available analytical methods?

Total chromium concentrations of 0.2 µg/L can be reliably reported by USEPA Method 200.8, or Standard Methods 3125 and EPA Method 200.9 respectively (USEPA 1994 and Standard Methods 1997). The UCMR3 requires acid digestion to minimize interferences that can arise due to carbon (e.g., alkalinity) in the water when measured by ICP/MS.

Hexavalent chromium can be measured at 0.02 µg/L using [Method 218.7](#) (USEPA 2011) or modified Method 218.6.

How should I collect and preserve the sample prior to analysis of total and hexavalent chromium?

Typically, samples are preserved in acid for the analysis of total metals in water. In the presence of particulates rigorous digestion is required to dissolve particles. Total chromium samples processed under the third Unregulated Contaminants Monitoring Rule must be preserved at a pH less than 2 using nitric acid and acid digested prior to analysis.

USEPA Method 218.7 for the analysis of hexavalent chromium calls for adjustment of the pH of the sample to greater than eight using ammonium sulfate/ ammonium hydroxide buffer or sodium carbonate/ammonium sulfate buffer. Using this method, USEPA allows for a maximum hold time of 14 days.

Treatment Technologies Information

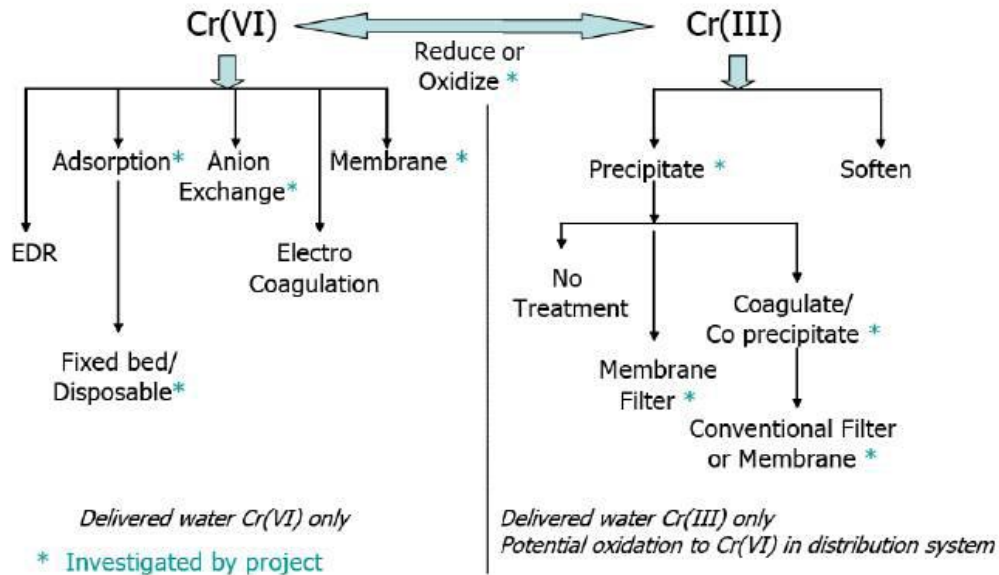
Will conventional treatment remove chromium from water?

A treatment profile survey presented in a WaterRF report (Frey 2004) showed that conventional treatment (coagulation + filtration) was able to remove trivalent chromium from water, but it did not remove hexavalent chromium. Removal of total chromium varied between 40% and 100% in the conventional surface water treatment systems that were profiled.

Removal of hexavalent chromium by conventional treatment (coagulation or lime softening followed by filtration) was investigated in bench-scale tests in a WaterRF study (Brandhuber 2004). The study observed that hexavalent chromium was not removed by alum or ferric coagulation or by lime softening. This can be attributed to high solubility of chromate and dichromate ions.

What treatment methods can be used for removing hexavalent chromium from drinking water?

Hexavalent chromium in water can be treated in one of two ways: 1) direct removal of hexavalent chromium, or 2) reduction of hexavalent chromium to the trivalent form, followed by removal of trivalent chromium. Two technologies have been tested and found to be successful at the demonstration-scale (Blute (2010), Blute and Wu, (2012)) and pilot-scale (McGuire et al. (2006), McGuire et al. (2007), Qin et al. (2005)) in Glendale, Calif., including reduction coagulation filtration (RCF) and single use weak base anion exchange (WBA). Strong base anion exchange (SBA) has been tested at the pilot-scale (McGuire et al., 2006). All three technologies can achieve Cr(VI) concentrations less than 1 ppb. Targeting total Cr removal with the WBA process to less than 1 ppb is very costly compared with operating to achieve Cr(VI) removal, but can be achieved. RCF with microfiltration rather than granular media filtration was necessary to target total chromium concentrations of less than 1 ppb in demonstration testing. The evaluation of removals to lower levels has continued and is still underway in Glendale. Information collected through the Glendale studies has been sufficiently detailed to support development of basic cost models for RCF and WBA (Najm, 2013) and analyze management options for residual streams from these treatment technologies (Blute and Wu, 2012).



Prior to the pilot- and demonstration-scale testing at Glendale, Calif., in 2004, a WaterRF study (Brandhuber et al, 2004) investigated a wide range of available treatment technologies through bench-scale experiments.

Figure 1: Treatment Technologies Tested for Chromium Removal from Drinking Water at the Bench-Scale (Brandhuber et al, 2004) In addition to the weak and strong base anion exchange (WBA and SBA) and RCF technologies that have been tested at demonstration scale, the bench-scale work indicated that high-pressure membranes (reverse osmosis and nanofiltration) and reduction / precipitation / adsorption via sulfur modified iron media may hold promise for Cr(VI) and Cr(III) removal. Neither have been tested specifically for Cr(VI) removal on a large scale.

How is hexavalent chromium reduced to the trivalent form for removal through conventional treatment?

A WaterRF study (Brandhuber 2004) evaluated ferrous salts as well as stannous chloride for the reduction of hexavalent chromium to its trivalent form. Both salts were able to achieve rapid and complete reduction of hexavalent chromium. Reduction of hexavalent chromium by sulfide and sulfite was rapid but complete reduction was not achieved. The reduction of hexavalent chromium to the trivalent form was also favored at a lower (acidic to near neutral) pH compared to alkaline pH conditions. Removal of Cr(III) rather than reduction must also be considered when removing Cr(VI) from drinking water, since Cr(III) can be reoxidized to Cr(VI) during treatment and in the distribution system (see below).

Does trivalent chromium convert to hexavalent chromium in drinking water distribution systems?

If an oxidant like the disinfectants used in drinking water treatment and distribution is present, trivalent chromium may be oxidized to the hexavalent form, partially or completely. A WaterRF study (Brandhuber et al, 2004) evaluated the effects of free chlorine, chloramines, potassium permanganate and hydrogen peroxide in the oxidation of trivalent chromium to the hexavalent species. Free chlorine could oxidize 50 – 65% of trivalent to hexavalent chromium at neutral or low pH conditions. However, the presence of other ions and natural organic matter may lessen the re-oxidation of Cr(III) by chlorine (Clifford and Chau, 1987). The Water Research Foundation is currently

funding research to explore the fate of trivalent as well as hexavalent chromium through treatment and the distribution system. A detailed discussion of the chemistry of chromium in drinking water treatment is available through the Water Research Foundation ([McNeil, 2012](#)).

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