ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA
CHROMIUM VI (HEXAVALENT CHROMIUM) ENTRY

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Like a library or most large databases (such as EPA's national STORET water quality database), this document contains information of variable quality from very diverse sources. In compiling this document, mistakes were found in peer reviewed journal articles, as well as in databases with relatively elaborate quality control mechanisms [366,649,940]. A few of these were caught and marked with a "[sic]" notation, but undoubtedly others slipped through. The [sic] notation was inserted by the editors to indicate information or spelling that seemed wrong or misleading, but which was nevertheless cited verbatim rather than arbitrarily changing what the author said.

Most likely additional transcription errors and typos have been added in some of our efforts. Furthermore, with such complex subject matter, it is not always easy to determine what is correct and what is incorrect, especially with the "experts" often disagreeing. It is not uncommon in scientific research for two different researchers to come up with different results which lead them to different conclusions. In compiling the Encyclopedia, the editors did not try to resolve such conflicts, but rather simply reported it all.

It should be kept in mind that data comparability is a major problem in environmental toxicology since laboratory and field methods are constantly changing and since there are so many different "standard methods" published by EPA, other federal agencies, state agencies, and various private groups. What some laboratory and field investigators actually do for standard operating practice is often a unique combination of various standard protocols and impromptu "improvements." In fact, the interagency task force on water methods concluded that [1014]:

> It is the exception rather than the rule that water-quality monitoring data from different programs or time periods can be compared on a scientifically sound basis, and that...
>
> No nationally accepted standard definitions exist for water quality parameters. The different organizations may collect data using identical or standard methods, but identify them by different names, or use the same names for data collected by different methods [1014].

Differences in field and laboratory methods are also major issues related to (the lack of) data comparability for chromium in media other than water: soil, sediments, tissues, and air.

In spite of numerous problems and complexities, knowledge is often power in decisions related to chemical contamination. It is therefore often helpful to be aware of a broad universe of conflicting results or conflicting expert opinions rather than having a portion of this information arbitrarily censored by someone else. Frequently one wants to know of the existence of information, even if one later decides not to use it for a particular application. Many would like to see a high percentage of the information available and decide for themselves what to throw out, partly because they don't want to seem uniformed or be caught by surprise by potentially important information. They are in a better position if they can say: "I knew about that data, assessed it based on the following quality assurance criteria, and decided not to use it for this application." This is especially true for users near the end of long decision processes, such as hazardous site cleanups, lengthy ecological risk assessments, or complex natural resource damage assessments.

For some categories, the editors found no information and inserted the phrase "no information found." This does not necessarily mean that no information exists; it simply means that during our efforts, the editors found none. For many topics, there is probably information "out there" that is not in the Encyclopedia. The more time that passes without encyclopedia updates (none are planned at the moment), the more true this statement will become. Still, the Encyclopedia is unique in that it contains broad ecotoxicology information from more sources than many other reference documents. No updates of this document are currently planned. However, it is hoped that most of the information in the encyclopedia will be useful for some time to come even with out updates, just as one can still find information in the 1972 EPA Blue Book [12] that does not seem well summarized anywhere else.

Although the editors of this document have done their best in the limited time available to insure accuracy of quotes as being "what the original author said," the proposed interagency funding of a bigger project with more elaborate peer review and quality control steps never materialized.

> The bottom line: The editors hope users find this document useful, but don't expect or depend on perfection herein. Neither the U.S. Government nor the National Park Service make any claims that this document is free of mistakes.

The following is one chemical topic entry (one file among 118). Before utilizing this entry, the reader is strongly encouraged to read the README file (in this subdirectory) for an introduction, an explanation of how to use this document in general, an explanation of how to search for power key section headings, an explanation of the organization of each entry, an information quality discussion, a discussion of copyright issues, and a listing of other entries (other topics) covered.

See the separate file entitled REFERENC for the identity of numbered references in brackets.

HOW TO CITE THIS DOCUMENT: As mentioned above, for critical applications it is better to obtain and cite the original publication after first verifying various data quality assurance concerns. For more routine applications, this document may be cited as:

> **Irwin, R.J., M. VanMouwerik, L. Stevens, M.D. Seese**, and **W. Basham.** 1997. Environmental Contaminants Encyclopedia. National Park Service, Water Resources Division, Fort Collins, Colorado. Distributed within the Federal Government as an Electronic Document (Projected public availability

on the internet or NTIS: 1998).

Chromium VI (Hexavalent Chromium Ion, CAS number 18540-29-9)

NOTE: This entry contains mostly information on Chromium VI. However, some information on elemental chromium and chromium III was also included when it was considered helpful. For much more detailed information on elemental chromium and chromium III, see the entries entitled Chromium and Chromium III.

Brief Introduction:

Br.Class: General Introduction and Classification Information:

Chromium (Cr) is a metallic element which is listed by the Environmental Protection Agency as one of 129 priority pollutants [58]. Chromium is considered one of the 14 most noxious heavy metals [83].

Chromium does not occur free in nature; in bound form it makes up 0.1-0.3 parts per million of the Earth's crust [343]. Trace quantities of certain forms of chromium are considered helpful or necessary [366,483].

Elemental chromium is very stable, but is not usually found pure in nature [24]. Chromium can exist in oxidation states ranging from -2 to +6, but is most frequently found in the environment in the trivalent (Cr+3) and hexavalent (Cr+6) oxidation states [24]. The +3 and +6 forms are the most important because the +2, +4, and +5 forms are unstable and are rapidly converted to +3, which in turn is oxidized to +6 [24].

Chromium compounds are stable in the trivalent state and occur in nature in this state in ores, such as ferrochromite ($FrCr2O4$). The hexavalent state is the second most stable state. However, hexavalent chromium rarely occurs naturally, but is produced from anthropogenic sources [927]. Hexavalent chromium occurs naturally in the rare mineral crocoite [927]. In the earth's crust, both trivalent and hexavalent chromium occur as dissolved chromium [190].

Br.Haz: General Hazard/Toxicity Summary:

Information on potential hazards of hexavalent chromium (Cr+6):

Many chromium compounds with a valence of 6 are called chromates, dichromates, or chromic acid; most have a yellow color, and all are toxic [343,751]. Hexavalent chromium compounds tend to be oxidizers and are associated with cancer risk and kidney damage [751].

Hexavalent chromium is more toxic than the +3 form because its oxidizing potential is high [24,751,929] and it easily penetrates biological membranes [24]. Chromium +6 is unstable [24] and can be reduced to chromium +3 by many oxidizing agents [751]. Metallic and acidic +6 chromates and dichromates tend to be strong oxidizing agents [751]. Strong oxidizing agents can cause damage to DNA and many other tissue structures.

Certain hexavalent chromium (Cr+6) compounds when administered via inhalation at high doses have the potential to induce lung tumors in humans and experimental animals [929]. However, at low levels of exposure hexavalent chromium ions are reduced in human bodily fluids such as gastric juice, epithelial lining fluid of the respiratory tract, blood, and other fluids, before the 6+ ions can interact with DNA, unless the dose is sufficient to overwhelm the body's reduction capacity [929].

Rainbow trout exposed to excessive hexavalent chromium developed severe gill damage precipitated by hypertrophy and hyperplasia [445]. Toxicity in aquatic species is known to be affected by water hardness, pH, temperature, species, and organism size [445]. Hard water conditions promote the toxicity of hexavalent chromium [445]. For many metals, alkalinity is sometimes a more important co-factor for toxicity than hardness (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

Hexavalent chromium is easily sorbed by gut or body walls (such as shells, gills, and mantle) because of its higher solubility [445].

At higher concentrations, Cr+6 is associated with abnormal enzyme activities, altered blood chemistry, lowered resistance to pathogenic organics, behavioral modifications, disrupted feeding, histopathology, osmoregularatory upset, alterations in population structure and species diversity indices, and inhibition of photosynthesis [24].

There may be some partial exceptions to the generalization that hexavalent chromium is more hazardous than trivalent. One author stated that fish are sometimes more sensitive to Cr+3 than to Cr+6 [926]. Another stated that in soft water, trivalent chromium is more toxic to fish than Cr+6 [445]. The mean 96-h LC50 for Cr+3 has been reported to be about four-fold lower than that for

Cr+6 in salmonid fish, with their reproductive cycles being particularly sensitive to Cr+3 [926]. However, the data are mixed and there appear to cases where chromium 6 is as hazardous or more hazardous to fish (and certainly to aquatic life other than fish) as chromium 3:

> A comparison of the lowest EC20 value for fish in general shows that the value for chromium 6 (51 ug/L) is lower than the value for chromium 3 (89 ug/L [649]. The lowest chronic values for fish in general shows little difference between chromium 6 (73.18 ug/L) vs. chromium 3 (68.63 ug/L) [649]. Both the acute and chronic national ambient water quality criteria for chromium 6 are much lower concentrations than the equivalent concentrations for chromium 3 [649].

Information on chromium in general (provided for comparison with the above text; see also Chromium entry):

The USEPA regards all chromium compounds as toxic, although the most toxic and carcinogenic chromium compounds tend to be the strong oxidizing agents with an oxidation state of +6 [751]. Divalent and trivalent forms of chromium have a (relatively) low order of toxicity [445,480]. The overall toxicity, carcinogenicity, and general hazard of chromium is highly related to chemical speciation [233,751]. The biological effects of chromium depend on chemical form, solubility and valence [24,751].

The toxic mechanism of action differs for hexavalent versus trivalent chromium [445]. Hexavalent chromium causes cellular damage via its role as a strong oxidizing agent, whereas trivalent chromium can inhibit various enzyme systems or react with organic molecules [445]. In mammalian species, chromium is considered one of the least toxic trace elements, as normal stomach pH converts hexavalent chromium to trivalent chromium [445]. One hundred to two hundreds times the normal total body load of chromium can usually be tolerated in mammals without evidence of negative effects [445]. The therapeutic:toxic dose ratio for trivalent chromium in rats has been calculated at approximately 1:10,000 [445].

As in the case of other metals, the overall hazard presented by chromium may be partly related to the solubility of the specific form of chromium [751]. Substances having a low solubility in water are often not as easily absorbed through the gastrointestinal tract as are those substances with higher solubilities [751]. Thus, chromium III fluoride, which is very insoluble (sic, actually "relatively insoluble") in water, is far less toxic than chromium III sulfate, which is much more soluble [751]. In the same way, some hexavalent chromium compounds tend to be more toxic than the +3 forms not only because the oxidizing potential of +6 compounds is high [24,751,929], but also because some of the +6 forms more easily penetrate biological membranes [24].

Chromium III, the naturally occurring form, has low toxicity due to poor membrane permeability and noncorrosivity, while Cr VI, from industrial emissions, is highly toxic due to strong oxidation characteristics and ready membrane permeability (Nat'l Research Council Canada; Effects of Chromium in the Canadian Envir p.15, 1976, NRCC No.15017) [609].

Both chromium III and VI (especially hexavalent) are significant from the standpoint of potential impacts to fish and wildlife [24,57]. However, although chromium in general has some notoriety as a potentially harmful environmental contaminant, most of that notoriety is due to the toxic, carcinogenic, oxidizing agent, general, and reproductive risk hazards of hexavalent chromium (Cr6+, chromium +6, chromate) compounds [366,480,483,751,929].

Little is known about the relation between concentrations of total chromium in a given environment and biological effects on the organisms living there [24]. Since the valence states of chromium are subject to change, tissues are often analyzed for total chromium. During the laboratory digestion of tissue samples, most chromium is changed to the trivalent form. Depending on the physical and chemical state of the Cr, the same elemental concentration has a wide variety of mobilities and reactivities and thus has different effects [24]. Chromium toxicity to aquatic biota is significantly influenced by abiotic variables such as hardness, temperature, pH, and salinity of water; and biological factors such as species, life stage, and potential differences in sensitivities of local populations [24]. Sensitivity to chromium varies widely, even among closely related species (that is, biota) [24].

The greatest chromium toxicity risk to plants is posed in acidic sandy soil with low organic content

[366]. In plants, chromium interferes with uptake translocation, and accumulation by plant tops of calcium, potassium, magnesium, phosphorus, boron, copper and aggravates iron deficiency chlorosis by interfering with iron metabolism [366].

Freshwater fish can regulate chromium over a wide range of ambient concentrations [180]. Some have even stated that freshwater fish seem to be relatively tolerant of chromium, although some aquatic invertebrates are very sensitive [302,375]. Organic forms of chromium with toxicological significance have not been found in nature [445].

Specific chromium compounds are quite toxic but the element itself has moderate to low toxicity [83] and acute poisoning from excess chromium is rare in humans [173]. The carcinogenic risk and oxidizing agent hazard from hexavalent (chromium +6) compounds, however may be significant [751].

Polychaete worms, clams, crabs, oysters, and fish have been shown to take up chromium; excess chromium in these species leads to decreased weight gain, increased oxygen consumption, impaired reproduction, and increased hematocrit [445].

Several comprehensive reports on the hazards of chromium, including Cr+3 and Cr+6, are available. Chromium hazards to fish and wildlife are summarized in Eisler's 1986 synoptic review [24]. Environment Canada has prepared a priority substances list assessment report for chromium [926]. ATSDR has prepared a toxicological profile for chromium which presents health effects via various exposure routes [927]. Due to a lack of time, important highlights from these documents have not yet been completely incorporated into this entry.

Br.Car: Brief Summary of Carcinogenicity/Cancer Information:

EPA 1996 IRIS information [893]:

Evidence for classification as to human carcinogenicity; weight-of-evidence classification

Classification: A; human carcinogen [893].

BASIS: Results of occupational epidemiologic studies of chromium-exposed workers are consistent across investigators and study populations. Dose-response relationships have been established for chromium exposure and lung cancer. Chromium-exposed workers are exposed to both chromium III and chromium VI compounds. Because only chromium VI has been found to be carcinogenic in animal studies, however, it was concluded that only chromium VI should be classified as a human carcinogen.

HUMAN CARCINOGENICITY DATA: Sufficient [893].

ANIMAL CARCINOGENICITY DATA: Sufficient. Hexavalent chromium compounds were carcinogenic in animal assays producing the following tumor types: intramuscular injection site tumors in Fischer 344 and Bethesda Black rats and in C57BL mice (Furst et al., 1976; Maltoni, 1974, 1976; Payne, 1960; Heuper and Payne, 1959); intraplural implant site tumors for various chromium VI compounds in Sprague-Dawley and Bethesda Black rats (Payne, 1960; Heuper 1961; Heuper and Payne, 1962); intrabronchial implantation site tumors for various Cr VI compounds in Wistar rats (Levy and Martin, 1983; Laskin et al., 1970; Levy as quoted in NIOSH, 1975); and subcutaneous injection site sarcomas in Sprague-Dawley rats (Maltoni, 1974, 1976) [893].

Some salts of chromium are carcinogenic [168] and humans exposed to chromium fumes have an increased risk for lung cancer [173].

The cancer mortality in Mancuso (1975) was assumed to be due to Cr VI, which was further assumed to be no less than one-seventh of total chromium [893].

Under appropriate conditions, Cr is a human and animal carcinogenic agent; its biological effects depend on chemical form, solubility and valence [24]. In general, Cr+6 compounds are hazardous to animals, whereas metallic Cr and Cr+3 are essentially non-toxic; however, exposure to water solubilized Cr+3 has caused cancers and dermatitis in workers, and toxicity in rabbits [24]. Inhalation of Cr+6 compounds may cause bronchial carcinomas in humans [24].

Based on the weight of the evidence of carcinogenicity in occupationally exposed populations, the group of hexavalent chromium compounds as a whole (since available data do not permit an assessment of individual compounds within the group) is classified as "carcinogenic to humans" (that is, as substances for which there is believed to be some chance of adverse health effects at any level of exposure) [926].

More than 100 years have passed since the first cancer case in a chromium worker was reported in Scotland....All chromium VI compounds should be considered carcinogenic, but no evidence has been presented indicating that human exposure to chromium III is associated with increased cancer risk. Zinc chromate is a potent carcinogen and calcium chromate may be a potent carcinogen. Evidence also suggests that water-soluble chromates in general may be more potent carcinogens than those with low solubility [Langard S. 1990. One hundred years of chromium and cancer: a review of epidemiological evidence and selected case reports. Am-J-Ind-Med 17(2); P 189-215, Department of Occupational Medicine, Telemark Central Hospital, Porsgrunn, Norway].

Br.Dev: Brief Summary of Developmental, Reproductive, Endocrine, and Genotoxicity Information:

Under laboratory conditions, chromium is mutagenic, carcinogenic, and teratogenic to a wide variety of organisms, and Cr+6 has the greatest biological activity [24]. Aquatic plants and marine polychaete worms appear to be the most sensitive groups tested. In exposures to Cr+6, growth of algae was inhibited at 10.0 ppb, and reproduction of worms at 12.5 ppb [24].

The reproductive effects seen in mice after oral dosing suggest a potential for chromium VI and chromium III to produce reproductive effects in humans exposed by the oral route. Levels of chromium found in drinking water and food, however, are probably not high enough to elicit reproductive effects in humans [927].

Hexavalent chromium compounds have been consistently positive in several genotoxicity assays in nonmammalian systems and in vitro and in vivo mammalian systems, inducing DNA damage, gene mutation, sister chromatid exchange, chromosomal aberrations, aneuploidy, cell transformation, and dominant lethal mutations [926].

In a study of a freshwater fish, Clarias batrachus, chromium did not cause any changes of protein concentration in the kidney and testis. In general, the biochemical parameters of the organs were affected by treatments of cations in the following order: cadmium > copper > chromium over control values of Clarias batrachus (Jana S, Sahana SS; Physiol Bohemoslov 37, 1: 79-82, 1988) [366].

One article reviewed approximately 700 results reported in the literature with 32 chromium compounds assayed in 130 short-term tests, using different targets and/or genetic end-points. The large majority of the results obtained with Cr VI compounds were positive, as a function of Cr VI solubility and bioavailability to target cells. On the other hand, Cr III compounds, although even more reactive than Cr VI with purified nucleic acids, did not induce genotoxic effects in the majority of studies using intact cells. Coupled with the findings of metabolic studies, the large data-base generated in short-term test systems provides useful information for predicting and interpreting the peculiar patterns of Cr VI carcinogenicity [De Flora S; Bagnasco M; Serra D; Zanacchi P, 1990. Genotoxicity of chromium compounds. A review. Mutat-Res; 1990 Mar; 238(2); P 99-172. Institute of Hygiene and Preventive Medicine, University of Genoa, Italy].

Br.Fate: Brief Summary of Key Bioconcentration, Fate, Transport, Persistence, Pathway, and Chemical/Physical Information:

In natural waters, chromium is commonly precipitated as (relatively) insoluble chromium hydroxide, formed from the reaction of trivalent chromium with aqueous hydroxide ion [445]. In waters where conditions favor the formation of hexavalent chromium, chromium will remain in solubilized form [445].

Since Cr+3 forms highly insoluble oxides, hydroxides, and phosphates, and is adsorbed by suspended particles, dissolved Cr+3 is removed rapidly from surface waters by settling particulate matter. However, Cr+3 can also form stable complexes with many dissolved or colloidal organic, and inorganic ligands. This complexed Cr+3 is relatively unaffected by adsorbtion and precipitation reactions, and can thus remain in the water column [926].

Although there are few oxidants capable of converting Cr+3 and Cr+6, and the oxidation kinetics are normally very slow, it has recently been suggested that unstable (including dissolved and colloidal) forms of Cr+3 can be converted to Cr+6 relatively quickly by strong oxidants such as H_2O_2 that are produced photochemically in aerobic surface waters [926].

Due to its association with suspended particulate phases, a large proportion of the Cr+3 discharged to surface water is transferred to sediment. In aerobic sediments, some Cr+3 can be oxidized by manganese oxides and hydroxides present at the sediment-water interface. It has been suggested that the resulting Cr+6 can be released to the overlying waters, especially by bioturbation processes [926].

In contrast to Cr+3, Cr+6 is not readily adsorbed to surfaces and, since most of its salts are soluble, much of the Cr+6 released to aerobic surface waters is present in a soluble form as hydrochromate, chromate, and dichromate ionic species [926]. However, dissolved Cr+6 can be converted to Cr+3 by a host of reducing agents such as S(2-), Fe(II), fulvic acid, low molecular weight organic compounds, and proteins, and is thus removed from solution, especially in deeper anaerobic waters [926]. Effectiveness of reducing agents varies with pH, redox conditions, and total concentrations of chromium. A small amount of Cr+6 can also be taken up by plankton and released as Cr+3 at lower depths where oxygen is depleted [926].

One strategy for remediation of hexavalent chromium in soils or sediments is to provide additional reducing agents (such as organic matter) to facilitate the conversion of relatively soluble Chromium +6 to relatively insoluble (and thus less mobile) chromium +3 [445].

Chromium is released to the atmosphere primarily in particulate form [926]. Since airborne chromium is associated mostly with the particulate phases, it is removed from the atmosphere by both dry fallout and wet precipitation. The residence time of chromium in the atmosphere is estimated to be less than 14 days [926].

Synonyms/Substance Identification:

Chromium (VI) [617]
Chromium (VI) ion [617]
Cr+6 [617]
Chromium (+6)
Chromium (+6) ion [617]
Chromium hexavalent ion [617]

Associated Chemicals or Topics:

See also individual entries:

Chromium III
Chromium

Water Data Interpretation, Concentrations and Toxicity (All Water Data Subsections Start with "W."):

W.Low (Water Concentrations Considered Low):

No information found.

W.High (Water Concentrations Considered High):

In White Oak Lake (Eastern Tennessee), which received chronic inputs of chromates from cooling towers located on two tributary streams, typical Cr+6 concentrations of

3 to 10 ppm in water effluents produced 100 to 300 ppb of Cr+6 in White Oak Lake vs. 5 ppb in a control area [24].

W.Typical (Water Concentrations Considered Typical):

California, 1986: Ambient background level for water concentrations of chromium +6 was 0.5 ug/l [222].

Control areas near White Oak Lake (Eastern Tennessee) contained 5 ppb Cr+6 [24].

W.Concern Levels, Water Quality Criteria, LC50 Values, Water Quality Standards, Screening Levels, Dose/Response Data, and Other Water Benchmarks:

W.General (General Water Quality Standards, Criteria, and Benchmarks Related to Protection of Aquatic Biota in General; Includes Water Concentrations Versus Mixed or General Aquatic Biota):

The lowest ambient water quality criteria (which one not specified) is 10.5 ug/L [1001,1003]. This is close the the IRIS value for Chronic Freshwater criterion: 1.1E+1 ug/L 4-day avg. [893].

Notes on total vs. acid soluble vs. dissolved metals:

Although most of the lab tests done to develop water quality criteria and other benchmarks were originally based on "total" values rather than "dissolved" values, some regulatory authorities nevertheless recommend comparing criteria with dissolved or acid soluble metals concentrations. EPA gave many reasons why water quality criteria should be compared to acid soluble values. For detailed discussions including EPA conversion factors for total vs. dissolved values, see the Laboratory and/or Field Analyses section (far below).

EPA 1996 IRIS information [893]:

Ambient Water Quality Criteria for Aquatic Organisms

Acute Freshwater: 1.6E+1 ug/L 1 hour avg. [893].

Older reference to same value: Water Quality Criteria in ug/L for CHROMIUM (VI) (CAS 18540-29-9) [446]: Freshwater Acute Criteria:

16 ug/L [446].

Chronic Freshwater: 1.1E+1 ug/L 4-day avg. [893].

Older reference to same value: Freshwater Chronic Criteria: 11 ug/L [446].

Marine Acute: 1.1E+3 ug/L 1 hour avg. [893].

Older reference to same value: Marine Acute Criteria: 1100 ug/L [446].

Marine Chronic 5.0E+1 ug/L 4-day avg. [893].

Older reference to same value: Marine Chronic Criteria: 50 ug/L [446].

Reference: 50 FR 30784 (07/28/85) [893].

Contact: Criteria and Standards Division / OWRS / (202)260-1315 [893].

Discussion: Criteria were derived from a minimum data base on all forms of chromium consisting of acute and chronic tests on a variety of species. Requirements and methods are covered in the reference to the Federal Register. [893].

Oak Ridge National Lab, 1994: Ecological Risk Assessment Freshwater Screening Benchmarks for concentrations of contaminants in water [649]. To be considered unlikely to represent an ecological risk, field concentrations should be below all of the following benchmarks [649]:

For CAS 018540-29-9 CHROMIUM VI (ug/L):

NATIONAL AMBIENT WATER QUALITY CRITERION - ACUTE: 16 ug/L

NOTE: The above is a hardness dependent criterion (100 mg/L CaCO3 was used to calculate the above concentration).

NATIONAL AMBIENT WATER QUALITY CRITERION CHRONIC: 11 ug/L

NOTE: The above is a hardness dependent criterion (100 mg/L CaCO3 was used to calculate the above concentration).

SECONDARY ACUTE VALUE: No information found.

SECONDARY CHRONIC VALUE: No information found.

SENSITIVE SPECIES TEST EC20: 0.266 ug/L

POPULATION EC2O: 316 ug/L

A State of California recommendation based on direct toxicity was that 1.5 ug/L be the water quality criteria for chromium +6 (4.5 ug/l was an adverse effects level) [222].

Adverse effects of chromium to sensitive species have been documented at 10.0 ug/L (ppb) of Cr+6 and 30.0 ug/L of Cr+3 in freshwater and 5.0 of Cr+6 in saltwater [24].

The threshold concentration of Cr+6 for avoidance/preference reactions in rainbow trout (Oncorhynchus mykiss) was reported as 28 ug/L [926].

Note: Before citing a concentration as EPA's water quality criteria, it is prudent to make sure you have the latest one. Work on the replacement for the Gold Book [302] was underway in March of 1996, and IRIS is updated monthly [893].

W.Plants (Water Concentrations vs. Plants):

LOWEST CHRONIC VALUE - AQUATIC PLANTS: 2 ug/L [649].

W.Invertebrates (Water Concentrations vs. Invertebrates):

LOWEST CHRONIC VALUE - DAPHNIDS: 6.132 ug/L [649].

LOWEST TEST EC20 - DAPHNIDS: 0.5 ug/L [649].

LOWEST CHRONIC VALUE - NON-DAPHNID INVERTEBRATES: no information found [649].

The lowest identified LOEL (lowest observed effect level) for dissolved Cr+6 to freshwater organisms is a 7-day LOEL of 0.5 ug/L, for impaired reproduction in the daphnid, Ceriodaphnia reticulata. This value was divided by a factor of 10, to account for potential differences in laboratory and field conditions as well as differences in sensitivity among species, to obtain an estimated effects threshold of 0.05 ug Cr+6/L [926]. Median concentrations of chromium in surface waters from Lake Erie and Lake Ontario were 5 to 15 times greater than the estimated effects threshold for Cr+6 [926].

Other effect levels reported in chronic test were 1.5 to 2.5 ug of Cr+6/L for Daphnia magna (reduced survival and reproduction) and 1.5 ug of Cr+6/L for Daphnia pulex (reduced survival) [926].

W.Fish (Water Concentrations vs. Fish):

LOWEST CHRONIC VALUE - FISH: 73.18 ug/L [649].

LOWEST TEST EC20 - FISH: 51 ug/L [649].

Information from Moore [445]:

Broderius and Smith (1979) determined the 96-hour, 10-day, 20-day, and 30-day LC50 values for juvenile fathead minnows (Pimephales promelas) exposed to waterborne hexavalent chromium (as sodium dichromate). Water chemistry in these studies included hardness of 220 ppm (as calcium carbonate) and pH of 7.8. Values obtained were 33.2, 12.4, 5.99, and 4.36 ppm chromium+6, respectively.

The acute toxicity of waterborne hexavalent chromium (as potassium dichromate) to fathead minnows was investigated by Pickering (1980). Water chemistry in this study included hardness of ~209 ppm (as calcium carbonate) and pH of 7.5-8.2. The 96-hour LC50 was 36.9 ppm.

Pickering (1980) also studied the effects of waterborne hexavalent chromium to fathead minnows in chronic toxicity tests. Two generations of minnows were exposed to chromium+6 (as potassium dichromate) in 5 concentrations from 0.018 ppm to 3.95 ppm. Water chemistry in these studies included hardness of 209 ppm (as calcium carbonate) and pH of 7.5-8.2. Sixty-three percent of minnows in the highest chromium+6 exposure died within 9 weeks. Survival also was affected in the second generation of minnows, with only 12% of fish surviving 60 days of exposure to 3.95 ppm chromium+6. Survivability of first and second generation fish exposed to lower concentrations of chromium+6 were similar to controls. Growth rates were lower in all chromium+6 exposed first generation fish after 9 weeks; however, the effect appeared to be temporary. The overall growth of second generation fish was only affected by 3.95 ppm chromium+6. Egg production of surviving fish was not affected by any chromium+6 concentration. The author concluded that the maximum acceptable toxicant concentration (MATC) for fathead minnows in hard water lies between 1.0 and 3.95 ppm chromium+6.

LD50 values for freshwater channelfish (Nuria denricus) exposed to waterborne hexavalent chromium (as potassium dichromate) were determined by Abbasi and Soni (1984b). Thirty adult channelfish were placed in each of 14 aquaria (each with a control) containing chromium+6 concentrations from 0 to 100 ppm. Water chemistry in these studies included hardness of 4.0-5.0 ppm total hardness and 1.0-3.0 ppm calcium hardness, and pH of 6.1-6.3. The LD50 values for 24, 96, 288, 384, and 480 hours were 55.54, 28.93, 2.91, 2.67, and 1.72 ppm, respectively. Fish exposed to hexavalent chromium exhibited alterations in swimming and balancing behaviors, including loss of balance, erratic and rapid twisting movements, and a higher frequency of surfacing and vertical swimming compared to controls. A dose-response decrease in feed consumption was noted in fish exposed to 5-100 ppm chromium+6. The acute toxicity of waterborne hexavalent chromium (as sodium chromate) to 63-day-old striped bass (Morone saxatilis) was investigated by Palawski et al. (1985). The 96-hour median lethal concentration for chromium+6 was 28 ppm in soft water (40 ppm calcium carbonate and pH 8.1), 38 ppm in very hard water (285 ppm calcium carbonate and pH 7.9), and 58 ppm in saline (1 ppth) water (pH 7.9).

Birge et al. (1979) conducted chronic toxicity tests for waterborne chromium+6 (as chromium trioxide) to embryo-larval rainbow trout. Log probit analyses were used to determine the control adjusted LC1, LC10, and LC50 values. Trout were exposed to chromium+6 using static renewal procedures from fertilization through 4 days post-hatching (a 28-day period). Water chemistry in this study included hardness of 92-110 ppm (as calcium carbonate) and pH of 6.9-7.8. Fish were examined daily to determine the number of deaths and terata; teratogenic survivors were considered lethals in calculations. The LC1, LC10, and LC50 values were 21.5 ppb, 56.9 ppb, and 190 ppb, respectively.

The 96-hour LC50's for 5-month-old brook trout (Salvelinus fontinalis) and 14-month-old rainbow trout exposed to waterborne chromium+6 (as sodium dichromate) were determined by Benoit (1976). Water chemistry in these studies included hardness of 44-46 ppm (as calcium carbonate) and pH of 7-8. Values obtained were 59 ppm and 69 ppm hexavalent chromium for brook and rainbow trout, respectively.

Benoit (1976) also conducted a series of three experiments to determine the chronic toxicity of waterborne hexavalent chromium (as sodium dichromate) to brook trout and rainbow trout. Separate 8-month tests were conducted on brook trout (from the embryo to juvenile stage) and rainbow trout (from the alevin through juvenile stage). Brook trout were exposed to five concentrations of chromium+6 from 0.01-0.20 ppm and rainbow trout were exposed to five concentrations of chromium+6 from 0.10-1.56 ppm. Additionally, a 22-month toxicity study was conducted on brook trout (alevin through adult stage) to include effects on reproduction and offspring. In that experiment, fish were exposed to five waterborne concentrations of chromium+6 from 0.35-6.37 ppm for the first 3 months; thereafter, because of the death of all fish in the 2 highest concentrations, only 3 concentrations (0.35, 0.76, and 1.56 ppm hexavalent chromium) were included. All experiments maintained a control group exposed to a chromium+6 concentration of <0.01 ppm. Water chemistry in these studies included hardness of 45 ppm (as calcium carbonate) and pH of 7-8.

There appear to be some exceptions to the generalization that hexavalent chromium is more hazardous than trivalent. One author stated that fish are sometimes more sensitive to Cr+3 than to Cr+6 [926]. Another stated that in soft water, trivalent chromium is more toxic to fish than Cr+6 [445]. The mean 96-h LC50 for Cr+3 has been reported to be about four-fold lower than that for Cr+6 in salmonid fish, with their reproductive cycles being particularly sensitive to Cr+3 [926]. However, the data are mixed and there appear to cases where chromium 6 is as hazardous or more hazardous to fish (and certainly to aquatic life other than fish) as chromium 3:

> A comparison of the lowest EC20 value for fish in general shows that the value for chromium 6 (51 ug/L) is lower than the value for chromium 3 (89 ug/L [649]. The lowest chronic values for fish in general shows little difference between chromium 6 (73.18 ug/L) vs. chromium 3 (68.63 ug/L), and both the acute and chronic national ambient water quality criteria for chromium 6 are much lower concentrations than the equivalent concentrations for chromium 3 [649].

W.Wildlife (Water Concentrations vs. Wildlife or Domestic Animals):

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Wildlife derived from No-Observed-Adverse-Effect (NOAEL) levels (see Tis.Wildlife, B) section below for these). To be considered unlikely to represent an ecological risk, wet-weight field concentrations should be below the following benchmarks for each species present at the site [650]:

CAS 18540-29-9 CHROMIUM VI (AS POTASSIUM CHROMATE)

SPECIES	WATER CONCENTRATION (ppm)
Rat (test species)	0.00000
Short-tailed Shrew	42.15800
Little Brown Bat	72.86600
White-footed Mouse	27.24600
Meadow Vole	47.68500
Cottontail Rabbit	22.59500
Mink	23.43100
Red Fox	16.72200
Whitetail Deer	9.35600

Comment: Actually, the number of

significant figures for a benchmark value should never be more than one; even if these values have been taken directly from another report, they should be rounded; otherwise the impression is given of a level of accuracy that is simply unwarranted. The uncertainties are too large to justify such a fine distinction (Owen Hoffman, SENES Oak Ridge, Personal Communication, 1997).

W.Human (Drinking Water and Other Human Concern Levels):

EPA 1995 Region 9 Tap Water Preliminary Remediation Goal: 180 ug/L [868].

EPA has set the maximum level of Cr+3 and Cr+6 allowed in drinking water at 100 ug Cr/L [927]. According to the EPA, the following levels of Cr+3 and Cr+6 in drinking water are not expected to cause effects that are harmful to health: 1400 ug/L for 10 days of exposure to children, 240 ug/L for longer-term exposure to children, 840 ug/L for longer-term exposure for adults, and 120 ug/L for lifetime exposure of adults [927].

Drinking Water MCL 1996: 0.10 mg/L (100 ug/L) [952].

Information listed by EPA in 1996 (IRIS) for Chromium VI [893]:

Ambient Water Quality Criteria for Human Health

Water & Fish: 5.0E+1 ug/liter [446,893].

Older IRIS Recalculated (9/90) Criteria for Water and Organisms: 170 [446].

Fish Only: None [446,893].

Older IRIS Recalculated (9/90) Criteria for Organisms Only: 3400 [446].

Econ/Tech?: No, does not consider economic or technical feasibility Reference: 45 FR 79318 (11/28/80) [893].

Contact: Criteria and Standards Division

/ OWRS / (202)260-1315 [893].

Discussion: The WQC of 5.0E+1 ug/L is based on consumption of contaminated aquatic organisms and water. [893].

Four states have water quality standards of 0.05 mg/L for chromium 6, while many other states use that same concentration as a standard for total chromium [927].

Most other benchmarks are for total chromium not for Chromium VI:

EPA 1996 IRIS information [893]:

Maximum Contaminant Level Goal

Value: 0.1 mg/L total chromium Status/Year: Final 1991 Econ/Tech?: No, does not consider economic or technical feasibility Reference: 56 FR 3526 (01/30/91) [893].

Contact: Health and Ecological Criteria Division / (202)260-7571 Safe Drinking Water Hotline / (800)426-4791 [893].

Discussion: An MCLG of 0.1 mg/L for total chromium (Cr III and Cr VI) is based on the EPA's RfD methodology for Cr VI, the more toxic chromium species. The MCLG is based upon a DWEL of 0.17 mg/L calculated from available human and animal data and an assumed drinking water contribution of 20 percent. An uncertainty factor of 500 was applied. The MCLG also falls into the safe and adequate daily dietary intake range of 50 to 200 mg/day for Cr III established by the National Research Council in the National Academy of Sciences (NAS, 1989). [893].

Maximum Contaminant Level (MCL)

Value: 0.1 mg/L total chromium [893] Status/Year: Final 1991 Econ/Tech?: No, does not consider economic or technical feasibility Reference: 56 FR 3526 (01/30/91). [893].

Contact: Drinking Water Standards Division / OGWDW / (202)260-7575 Safe Drinking Water Hotline / (800)426-4791 [893].

Discussion: The EPA has established an MCL equal to the MCLG of 0.1 mg/L [893].

> Note: Before citing a concentration as EPA's water quality criteria, it is prudent to make sure you have the latest one. Work on the replacement for the Gold Book [302] was underway in March of 1996, and IRIS is updated monthly [893].

W.Misc. (Other Non-concentration Water Information):

There appear to be some exceptions to the generalization that hexavalent chromium is more hazardous than trivalent (see W.Fish and W.Invertebrates sections above).

As of January 1995, the U.S. EPA was recommending that states use dissolved measurements in water quality standards for metals. See Laboratory section below for recommended EPA generic conversion factors.

Sediment Data Interpretation, Concentrations and Toxicity (All Sediment Data Subsections Start with "Sed."):

Sed.Low (Sediment Concentrations Considered Low):

No information found.

Sed.High (Sediment Concentrations Considered High):

No information found.

Sed.Typical (Sediment Concentrations Considered Typical):

No information found.

Sed.Concern Levels, Sediment Quality Criteria, LC50 Values, Sediment Quality Standards, Screening Levels, Dose/Response Data and Other Sediment Benchmarks:

Sed.General (General Sediment Quality Standards, Criteria, and Benchmarks Related to Protection of Aquatic Biota in General; Includes Sediment Concentrations Versus Mixed or General Aquatic Biota):

No information found.

See also: Chromium entry.

Sed.Plants (Sediment Concentrations vs. Plants):

No information found.

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

No information found.

Sed.Fish (Sediment Concentrations vs. Fish):

No information found.

Sed.Wildlife (Sediment Concentrations vs. Wildlife or Domestic Animals):

No information found.

Sed.Human (Sediment Concentrations vs. Human):

No information found.

Sed.Misc. (Other Non-concentration Sediment Information):

No information found.

Soil Data Interpretation, Concentrations and Toxicity (All Soil Data Subsections Start with "Soil."):

Soil.Low (Soil Concentrations Considered Low):

No information found.

Soil.High (Soil Concentrations Considered High):

No information found.

Soil.Typical (Soil Concentrations Considered Typical):

No information found.

Soil.Concern Levels, Soil Quality Criteria, LC50 Values, Soil Quality Standards, Screening Levels, Dose/Response Data and Other Soil Benchmarks:

Soil.General (General Soil Quality Standards, Criteria, and Benchmarks Related to Protection of Soil-dwelling Biota in General; Includes Soil Concentrations Versus Mixed or General Soil-dwelling Biota):

Soil cleanup criteria for decommissioning industrial sites in Ontario for Chromium 6+ (1987): For residential and parklands chromium 6+ should not exceed 10 ppm, for commercial and industrial land chromium 6+ should not exceed 10 ppm [347].

See also: Chromium entry.

Soil.Plants (Soil Concentrations vs. Plants):

Although both Cr+3 and Cr+6 are equally available to plants grown in nutrient solutions, the results of most studies indicate that Cr+6 is consistently more toxic than Cr+3. When added to sandy soils, 5 ug/g dry wt of Cr+6 induced iron chlorosis in oats, retarded stem development in tobacco, and inhibited the uptake of micronutrients by soybeans [926].

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

No information found.

Soil.Wildlife (Soil Concentrations vs. Wildlife or Domestic Animals):

No information found.

Soil.Human (Soil Concentrations vs. Human):

EPA 1996 National Generic Soil Screening Level (SSL) designed to be conservative and protective at the majority of sites in the U.S. but not necessarily protective of all known human exposure pathways, land uses, or ecological threats [952]:

SSL = 390 mg/kg for ingestion pathway [952].

SSL = 270 mg/kg for inhalation pathway [952].

SSL = 2 to 38 mg/kg for protection from migration to groundwater at 1 to 20 Dilution-Attenuation Factor (DAF) [952].

EPA 1995 Region 9 Preliminary remediation goals (PRGs), 1995 [868]:

Residential Soil: 30 mg/kg wet wt.
Industrial Soil: 64 mg/kg wet wt.

NOTE:
1) PRGs focus on the human exposure pathways of ingestion, inhalation of particulates and

volatiles, and dermal absorption. Values do not consider impact to groundwater or ecological receptors.
2) Values are based on a non-carcinogenic hazard quotient of one.
3) PRGs for residential and industrial landuses are slightly lower concentrations than EPA Region III RBCs, which consider fewer aspects [903].

EPA 1995 Region 3 Risk based concentration (RBC) to protect from transfers to groundwater:

19 mg/kg dry weight [903].

Acceptable level of chromium for production of healthy food: 0.05 (value given for Cr6+ form) ppm dry weight (Moscow) [719].

Soil.Misc. (Other Non-concentration Soil Information):

No information found.

Tissue and Food Concentrations (All Tissue Data Interpretation Subsections Start with "Tis."):

Tis.Plants:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Plants:

No information found.

B) Body Burden Residues in Plants: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

No information found.

Tis.Invertebrates:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Invertebrates:

No information found.

B) Concentrations or Doses of Concern in Food Items Eaten by Invertebrates:

No information found.

C) Body Burden Residues in Invertebrates: Typical, Elevated, or of Concern Related to the Well-being of the

Organism Itself:

No information found.

Tis.Fish:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Fish (Includes FDA Action Levels for Fish and Similar Benchmark Levels From Other Countries):

No information found.

B) Concentrations or Doses of Concern in Food Items Eaten by Fish:

No information found.

C) Body Burden Residues in Fish: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

No information found.

Tis.Wildlife: Terrestrial and Aquatic Wildlife, Domestic Animals and all Birds Whether Aquatic or not:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Wildlife, Domestic Animals, or Birds:

No information found.

B) Concentrations or Doses of Concern in Food Items Eaten by Wildlife, Birds, or Domestic Animals (Includes LD50 Values Which do not Fit Well into Other Categories, Includes Oral Doses Administered in Laboratory Experiments):

Adverse effects of chromium to sensitive species of wildlife have been documented at 5.1 and 10.0 mg/kg of diet (ppm) of Cr+6 and Cr+3, respectively [24].

No adverse effects on survival and growth were observed in male domestic chickens exposed to 100 ug/g wet weight of Cr+6 in the diet for 32 days [926].

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Wildlife derived from No-Observed-Adverse-Effect (NOAEL) levels (mg contaminant per kg body weight per day). To be considered unlikely to represent an ecological risk, wet-weight field concentrations should be below the following (right column) benchmarks for each species present at the site [650]:

CAS 18540-29-9 CHROMIUM VI (AS POTASSIUM CHROMATE)

SPECIES	NOAEL (mg/kg/day)	FOOD CONCENTRATION (ppm)
Rat (test species)	3.28000	0.00000
Short-tailed Shrew	9.27500	15.45800
Little Brown Bat	11.65900	34.97600
White-footed Mouse	8.17400	52.88800
Meadow Vole	6.50200	57.22100
Cottontail Rabbit	2.18400	11.05900
Mink	2.32000	16.93200
Red Fox	1.41200	14.12100
Whitetail Deer	0.61300	19.89500

Comment: Actually, the number of significant figures for a benchmark value should never be more than one; even if these values have been taken directly from another report, they should be rounded; otherwise the impression is given of a level of accuracy that is simply unwarranted. The uncertainties are too large to justify such a fine distinction (Owen Hoffman, SENES Oak Ridge, Personal Communication, 1997).

C) Body Burden Residues in Wildlife, Birds, or Domestic Animals: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

No information found.

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

No information found.

B) Concentrations or Doses of Concern in Food Items Eaten by Humans (Includes Allowable Tolerances in Human Food, FDA, State and Standards of Other Countries):

RfD: 5E-3 mg/kg-day Confidence: Low [893,952].

RfD: 0.005 mg/kg/day [952].

Crit. Dose: 2.4 mg/kg-day [Study 1 NOAEL(adj)]
UF: 500 MF: 1 [993].

C) Body Burden Residues in Humans: Typical, Elevated, or of Concern Related to the Well-being of Humans:

No information found.

Tis.Misc. (Other Tissue Information):

In the body, chromium +6 can be reduced to chromium +3, but the reverse reaction does not occur (in the body) [483].

Bio.Detail: Detailed Information on Bioconcentration, Biomagnification, or Bioavailability:

No information found.

Interactions:

No information found.

Uses/Sources:

Chromium is used in a wide variety of industrial applications in Canada including the production of stainless and heat-resistant steels, refractory products such as bricks and mortars, and in pigments, metal finishing, leather tanning, and wood preservatives [926]. Both trivalent and hexavalent forms of chromium are released into the environment in Canada as a result of these industrial uses, as well as from the production and combustion of fossil fuels, and the smelting and refining of nonferrous base metals [926].

Chromium is widely used as a corrosion inhibitor in cooling waters by the electric power industry. Its use in this capacity involves addition of a Cr+6 salt, typically sodium dichromate, which forms an oxide on metal surfaces. Chromates are subsequently released to surface water in high concentrations, compared with background levels of Cr in most freshwaters [24].

Hexavalent chromium occurs naturally in the rare mineral crocoite [927].

Most of the chromium (+6) found in nature is a result of domestic and industrial emissions. The hexavalent state is the second most stable state. However, hexavalent chromium rarely occurs naturally, but is produced from anthropogenic sources [927].

Drinking water generally contains the same chromium levels as the surface and groundwaters, which serve as its source. Although some piping materials contain significant levels of chromium (corrosion resistant steel, 8-14%; cement, 5-120 ppm chromium), little is leached into the water. However, it should be noted that Cr III may be oxidized to Cr VI during the chlorination process (Nat'l Research Council Canada; Effects of Chromium in the Canadian Environment p.36, 1976, NRCC No 15017) [609].

Occupational exposure: chromium & its compounds are found in 3 main types of indust activity: (1) metallurgical, (2) use in refractory materials, and (3) many of highly colored chromate salts are used in pigment, paint, tanning & dyeing industries (IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT, Multivolume work, p. V23 243, 1980) [609].

Forms/Preparations/Formulations:

No information found.

Chem.Detail: Detailed Information on Chemical/Physical Properties:

No information found on Cr+6. See sources such as ATSDR for chemical/physical information of a variety of Cr+6 compounds [927].

Fate.Detail: Detailed Information on Fate, Transport, Persistence, and/or Pathways:

See Br.Fate section above for information on chromium VI. Additional information on chromium in general [609]:

TERRESTRIAL FATE: In order to decide on a suitable sampling depth for grassland soil treated with sewage sludge and to assess implications for grazing animals, a field trial on two soils was designed to estimate the distribution of metals in grassland soil profiles following surface applications of sludge. Soil cores were taken using specialized equipment to 30 cm depth and divided into seven sections. Movement from the soil surface to a depth of 10 cm was observed for all of the seven metals; cadmium, chromium, copper, molybdenum, nickel, lead and zinc, but most of the metal (60%-100%, mean 87%) remained in the upper 5 cm of soil. Sampling to a depth of 5 or 7.5 cm would be most suitable for monitoring long-term grassland treated with surface applications of sludge. [Davis RD et al: Environ Pollut 49 (2): 99-116 (1988)].

TERRESTRIAL FATE: Uptake is greater from ultrabasic soils by a factor of 5-40 than on calcarious or silica-based soils. /Total chromium/ [Schroeder HA et al; J Chron Dis 15: 941-4 (1962) as cited in NAS; Medical and Biological Effects of Environmental Pollutants: Chromium p.12 (1974)].

Aquatic Fate: ... Most of the chromium in surface waters may be present in particulate form as sediment. Some of the particulate chromium would remain as suspended matter and ultimately be deposited in sediments. ... The exact chemical forms of chromium in surface waters are not well defined. Although most of the soluble chromium in surface waters may be present as Cr VI, a small amount may be present as Cr III organic complexes. Hexavalent chromium is the major stable form of chromium in seawater;

> however, Cr VI may be reduced to Cr III by organic matter present in water, and may eventually deposit in sediments. /Chromium/ [USEPA; Health Assessment Document: Chromium p.3-18 (1984) EPA 600/8-83-014F].
>
> ATMOSPHERIC FATE: Chromium is associated with particulate matter in the air, and is not expected to exist in gaseous form. /Total chromium/ [Nat'l Research Council Canada; Effects of Chromium in the Canadian Envir p.22 (1976) NRCC No.15017].
>
> Atmospheric Fate: Chromium (Cr) is most highly concn in the smallest particles collected from ambient air. Bulk analysis does not allow adequate characterization of these particles. /Total chromium/ [Natusch DFS et al; Science 183: 202-4 (1974)].

Laboratory and/or Field Analyses:

Detection limits should be no higher than comparison benchmarks or criteria for various media (water, sediments, soil, tissues, etc), some of which are low (see sections above). The lowest ambient water quality criteria is 10 ug/L and the detection limit (MDL) is 0.23 ug/L using EPA method 1636, a 1996 ion chromatography (IC) method [1003]. Before the development of method 1636, EPA 218.4 was recommended by EPA (40 CFR Part 136, Table IB, 1994 edition of CFR Part 40) and method 218.6 was recommended in a separate EPA publication [1006].

Preservation recommendation for Chromium VI: Add 50% NaOH; preserve immediately after sample collection [1003]. Although NaOH is specified for preservation, when acid is used (presumably for other purposes) EPA method 1636 specifies use of nitric acid—concentrated (sp gr 1.41), Seastar or equivalent [1003].

Acceptable containers (after proper cleaning per EPA protocols) for Chromium VI: 500-mL or 1-L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid [1003].

As of January 1995, the U.S. EPA was recommending that states use dissolved measurements in water quality standards for metals, in concert with recommendations EPA previously made for the Great Lakes [672]. The conversion factors recommended by EPA for converting total recoverable metals criteria to dissolved metal criteria were given as follows [672]:

> Chromium +6 conversion for acute and chronic criteria are 0.988 and 0.966, respectively (for example, total recoverable metals acute criteria x 0.988 = dissolved metals acute criteria).

The conversion factors recommended by EPA for converting total recoverable Chromium VI to dissolved concentrations in the January 1997 draft EPA Guidelines for 5 year 305(B) assessments were:

0.982 for Criterion Maximum Concentration.

0.962 for Criterion Continuous Concentration.

> Note: None of these "generic" conversion factors work well for all areas. Both total and dissolved concentrations should be checked at new locations before relying on generic conversion factors (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

Holding times recommended for EPA for water samples of Chromium VI has been given as 24 hours (Federal Register, Volume 49, No. 209, Friday, October 28, 1984, page 43260). EPA also specified 24 hours in 1994 (40 CFR, Part 136.3, Table 2, page 397, 1994). Method 1636 states that:

> For dissolved Cr(VI) determinations, samples must be filtered through a 0.45-um capsule filter at the field site [1003]. The filtered samples should be preserved in the field; otherwise, samples must be analyzed within 24 h of collection [1003].

EPA method 1669, which is supposed to be used with method 1636 states:

> Field preservation can increase sample holding times for hexavalent chromium to 30 days; therefore it is recommended that preservation of samples for hexavalent chromium be performed in the field. For other metals, however, the sampling team may prefer to utilize laboratory preservation of samples to expedite field operations and to minimize the potential for sample contamination [1003]. Field preservation is not necessary for dissolved metals, except for trivalent and hexavalent chromium [1003]..... Field preservation is advised for hexavalent chromium in order to provide sample stability for up to 30 days [1003].

Method 1636 specifies "An aqueous sample is filtered through a 0.45-um filter and the filtrate is adjusted to a pH of 9 to 9.5 with a concentrated buffer solution. A measured volume of the sample (50–250 uL) is introduced into the ion chromatograph. A guard column removes organics from the sample before the Cr(VI), as CrO42-, is separated on a high capacity anion exchange separator column. Postcolumn derivatization of the Cr(VI) with diphenylcarbazide is followed by detection of the colored complex at 530 nm" [1003].

The degree to which a water sample is re-acidified, re-checked for pH, shaken before analysis, and the length of time it sits before and after these steps, seems to vary a lot between laboratories, and EPA guidance for various methods is not consistent.

For metals work in general, some labs recheck pH, some don't. Some shake, some don't, etc. Some collectors leave head space in jars, some don't. Neither the word "shake" nor the phrase head space appear in EPA method 1636.. Air from the atmosphere or in headspace can cause oxidation of anaerobic groundwater or anaerobic sediment samples. This oxidation can cause changes in chemical oxidation states of contaminants in the sample, so that the results are not typical of the anaerobic conditions which were present in the environment prior to sampling (John Benham, National Park Service, Personal Communication, 1997).

Since the valence states are subject to change, tissues are often analyzed for total chromium. During the laboratory digestion of tissue samples, most chromium is changed to the trivalent form. (Harzdorf AC; Int J Environ Anal Chem 29, 4: 249-61, 1987) [699].

Variation in concentrations of contaminants may sometimes be due to differences in how individual investigators treat samples in the field and lab rather than true differences in environmental concentrations. As of 1997, the problem of lack of data comparability (not only for water methods but also for soil, sediment, and tissue methods) between different "standard methods" recommended by different agencies seemed to be getting worse, if anything, rather than better. See also: discussion of comparability of data in the disclaimer section at the top of this entry.

In 1997, the trend in quality assurance seemed to be for various agencies, including the EPA and others, to insist on quality assurance plans for each project. In addition to quality control steps (blanks, duplicates, spikes, etc.), these quality assurance plans call for a step of insuring data comparability [1015,1017]. However, the data comparability step is often not given sufficient consideration. The tendency of agency guidance (such as EPA SW-846 methods and some other new EPA methods for bio-concentratable substances) to allow more and more flexibility to select options at various points along the way, makes it harder in insure data comparability or method validity. Even volunteer monitoring programs are now strongly encouraged to develop and use quality assurance project plans [1015,1017].

At minimum, before using contaminants data from diverse sources, one should determine that field collection methods, detection limits, and lab quality control techniques were acceptable and comparable. The goal is that the analysis in the concentration range of the comparison benchmark concentration should be very precise and accurate.

It should be kept in mind that quality control field and lab blanks and duplicates will not help in the data quality assurance goal as well as intended if one is using a method prone to false negatives. Methods may be prone to quality assurance problems due to the use of detection limits that are too high, the loss or addition of contaminants through inappropriate handling, or the use of inappropriate methods.

Highlights from EPA Method 1636: Determination of dissolved hexavalent chromium in ambient waters by ion chromatography [1003]:

As of March 1997, the EPA 1600 series methods had not yet been officially approved in 40 CFR for use in NPDES permits, but the improvements in these methods were suggested by EPA staff to be wise practice when attempting low detection limit analyses for metals.

This 1996 proposed EPA method is for the determination of dissolved hexavalent chromium (as CrO42-) in ambient waters at EPA water quality criteria (WQC) levels using ion chromatography (IC) [1003]. This method was developed by integrating the analytical procedures in EPA Method 218.6 with the quality control (QC) and sample handling procedures necessary to avoid contamination and ensure the validity of analytical results during sampling and analysis for metals at EPA WQC levels [1003]. This method contains QC procedures that will ensure that contamination will be detected when blanks accompanying samples are analyzed [1003]. This method is accompanied by Method 1669: Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels (the "Sampling Method") [1003]. The Sampling Method is necessary to ensure that contamination will not compromise trace metals determinations during the sampling process [1003].

For dissolved Cr(VI) determinations, samples must be filtered through a 0.45-um capsule filter at the field site [1003]. The Sampling Method describes the filtering procedures [1003]. The filtered samples should be preserved in the field; otherwise, samples must be analyzed within 24 h of collection [1003]. The Sampling Method details procedures for field preservation [1003].

Samples containing high levels of anionic species such as sulphate and chloride may cause column overload [1003]. Samples containing high levels of organics or sulfides cause rapid reduction of soluble Cr(VI) to Cr(III) [1003]. Samples must be stored at 4°C and analyzed within 24 h of collection unless preserved with sodium hydroxide [1003].

The lowest ambient water quality criteria is 10.5 ug/L and the detection limit (MDL) is 0.23 ug/L [1001,1003].

Specifies use of nitric acid—concentrated (sp gr 1.41), Seastar or equivalent [1003].

Preventing ambient water samples from becoming contaminated during the sampling and analytical process constitutes one of the greatest difficulties encountered in trace metals determinations [1003]. Over the last two decades, marine chemists have come to recognize that much of the historical data on the concentrations of dissolved trace metals in seawater are erroneously high because the concentrations reflect contamination from sampling and analysis rather than ambient levels [1003]. More recently, historical trace metals data collected from freshwater rivers and streams have been shown to be similarly biased because of contamination during sampling and analysis [1003]. Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing ambient water samples for trace metals [1003].

Samples may become contaminated by numerous routes [1003]. Potential sources of trace metals contamination during sampling include metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, sampling equipment, reagents, and reagent water; improperly cleaned and stored equipment, labware, and reagents; and atmospheric inputs such as dirt and dust [1003]. Even human contact can be a source of trace metals contamination [1003].

Philosophy—The philosophy behind contamination control is to ensure that any object or substance that contacts the sample is metal free and free from any material that may contain metals [1003].

Use a clean environment—The ideal environment for processing samples is a class 100 clean room [1003]. If a clean room is not available, all sample preparation should be performed in a class 100 clean bench or a nonmetal glove box fed by particle-free air or nitrogen [1003]. Digestions should be performed in a nonmetal fume hood situated, ideally, in the clean room [1003].

Minimize exposure—The Apparatus that will contact samples, blanks, or standard solutions should be opened or exposed only in a clean room, clean bench, or glove box so that exposure to an uncontrolled atmosphere is minimized [1003]. When not being used, the Apparatus should be covered with clean plastic wrap, stored in the clean bench or in a plastic box or glove box, or bagged in clean zip-type bags [1003]. Minimizing the time between cleaning and use will also minimize contamination [1003].

Clean work surfaces—Before a given batch of samples is processed, all work surfaces in the hood, clean bench, or glove box in which the samples will be processed should be cleaned by wiping with a lint-free cloth or wipe soaked with reagent water [1003].

Wear gloves—Sampling personnel must wear clean, nontalc gloves during all operations involving handling of the Apparatus, samples, and blanks [1003]. Only clean gloves may touch the Apparatus [1003]. If another object or substance is touched, the glove(s) must be changed before again handling the Apparatus [1003]. If it is even suspected that gloves have become contaminated, work must be halted, the contaminated gloves removed, and a new pair of clean gloves put on [1003]. Wearing multiple layers of clean gloves will allow the old pair to be quickly stripped with minimal disruption to the work activity [1003].

Construction materials—Only the following materials should come in contact with samples: fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, polypropylene, polysulfone, or ultrapure quartz [1003]. PTFE is less desirable than FEP because the sintered material in PTFE may contain contaminates and is susceptible to serious memory contamination [1003]. Stainless steel is a major source of chromium contamination [1003]. All materials, regardless of construction, that will directly or indirectly contact the sample must be cleaned using the procedures described in Section 11 and must be known to be clean and metal free before proceeding [1003].

The following materials have been found to contain trace metals and should not contact the sample or be used to hold liquids that contact the sample, unless these materials have been shown to be free of the metals of interest at the desired level: Pyrex, Kimax, methacrylate, polyvinylchloride, nylon, and Vycor [1003]. In addition, highly colored plastics, paper cap liners, pigments used to mark increments on plastics, and rubber all contain trace levels of metals and must be avoided [1003].

Reduction of Cr(VI) to Cr(III) can occur in the presence of reducing species in an acidic medium [1003]. At pH 6.5 or greater, however, CrO42-, which is less reactive than HCrO4-, is the predominant species [1003].

Hexavalent chromium is toxic and a suspected carcinogen and should be handled with appropriate precautions [1003]. Extreme care should be exercised when weighing the salt for preparation of the stock standard [1003].

All sampling equipment, sample containers, and labware should be cleaned in a designated cleaning area that has been demonstrated to be free of trace element contaminants [1003]. Such areas may include class 100 clean rooms as described by Moody, labware cleaning areas as described by Patterson and Settle, or clean benches [1003].

Highlights from EPA Field Method 1669 for Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels (To be used along with Lab method 1636 above) [1003]:

As of March 1997, the 1600 series methods had not yet been officially approved in 40 CFR for use in NPDES permits, but the improvements in these methods were suggested by EPA staff to be wise practice when attempting low detection limit analyses for metals.

This "field method details" protocol is for the collection and filtration of ambient water samples for subsequent determination of total and dissolved Antimony, Arsenic, Cadmium, Copper, Chromium III, Chromium VI, Lead, Mercury, Nickel, Selenium, Silver, Thallium, and Zinc, at low (Water Quality Criteria Range) concentrations [1003]. It is designed to support the implementation of water quality monitoring and permitting programs administered under the Clean Water Act [1003].

This method is not intended for determination of metals at concentrations normally found in treated and untreated discharges from industrial facilities [1003]. Existing regulations (40 CFR Parts 400–500) typically limit concentrations in industrial discharges to the mid to high part-per-billion (ppb) range, whereas ambient metals concentrations are normally in the low part-per-trillion (ppt) to low ppb range [1003]. This guidance is therefore directed at the collection of samples to be measured at or near the water quality criteria levels [1003]. Often these methods will be necessary in a water quality criteria-based approach to EPA permitting [1001]. Actual concentration ranges to which this guidance is applicable will be dependent on the sample matrix, dilution levels, and other laboratory operating conditions [1003].

The ease of contaminating ambient water samples with the metal(s) of interest and interfering substances cannot be overemphasized [1003]. This method includes sampling techniques that should maximize the ability of the sampling team to collect samples reliably and eliminate sample contamination [1003].

Clean and ultraclean—The terms "clean" and "ultraclean" have been used in other Agency guidance [1004] to describe the techniques needed to reduce or eliminate contamination in trace metals determinations [1003]. These terms are not used in this sampling method due to a lack of exact definitions [1003]. However, the information provided in this method is consistent with summary guidance on clean and ultraclean techniques [1004].

Preventing ambient water samples from becoming contaminated during the sampling and analytical process is the greatest challenge faced in trace metals determinations [1003]. In recent years, it has been shown that much of the historical trace metals data collected in ambient water are erroneously high because the concentrations reflect contamination from sampling and analysis rather than ambient levels [1003]. Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing ambient water samples for trace metals [1003].

There are numerous routes by which samples may become contaminated [1003]. Potential sources of trace metals contamination during sampling include metallic or metal-containing sampling equipment, containers, labware (e.g. talc gloves that contain high levels of zinc), reagents, and deionized water; improperly cleaned and stored equipment, labware, and reagents; and atmospheric inputs such as dirt and dust from automobile exhaust, cigarette smoke, nearby roads, bridges, wires, and poles [1003]. Even human contact can be a source of trace metals contamination [1003]. For example, it has been demonstrated that dental work (e.g., mercury amalgam fillings) in the mouths of laboratory personnel can contaminate samples that are directly exposed to exhalation [1003].

For dissolved metal determinations, samples must be filtered through a 0.45-um capsule filter at the field site [1003]. The filtering procedures are described in this method [1003]. The filtered samples may be preserved in the field or transported to the laboratory for preservation [1003].

This document is intended as guidance only [1003]. Use of the terms "must," "may," and "should" are included to mean that EPA believes that these procedures must, may, or should be followed in order to produce the desired results when using this guidance [1003]. In addition, the guidance is intended to be performance-based, in that the use of less stringent procedures may be used so long as neither samples nor blanks are contaminated when following those modified procedures [1003]. Because the only way to measure the performance of the modified procedures is through the collection and analysis of uncontaminated blank samples in accordance with this guidance and the referenced methods, it is highly recommended that any modifications be thoroughly evaluated and demonstrated to be effective before field samples are collected [1003].

The method includes a great many details regarding prevention of field contamination of samples, including clothing needed, clean hands vs. dirty hands operations, and numerous other details [1003].

Surface sampling devices—Surface samples are collected using a grab sampling technique [1003]. Samples may be collected manually by direct submersion of the bottle into the water or by using a grab sampling device [1003]. Grab samplers may be used at sites where depth profiling is neither practical nor necessary [1003].

An alternate grab sampler design is available [1003]. This grab sampler is used for discrete water samples and is constructed so that a capped clean bottle can be submerged, the cap removed, sample collected, and bottle recapped at a selected depth [1003]. This device eliminates sample contact with conventional samplers (e.g., Niskin bottles), thereby reducing the risk of extraneous contamination [1003]. Because a fresh bottle is used for each sample, carryover from previous samples is eliminated [1003].

Subsurface sampling devices—Subsurface sample collection may be appropriate in lakes and sluggish deep river environments or where depth profiling is determined to be necessary [1003]. Subsurface samples are collected by pumping the sample into a sample bottle [1003]. Examples of subsurface collection systems include the jar system device or the continuous-flow apparatus [1003].

Advantages of the jar sampler for depth sampling are (1) all wetted surfaces are fluoropolymer and can be rigorously cleaned; (2) the sample is collected into a sample jar from which the sample is readily recovered, and the jar can be easily recleaned; (3) the suction device (a peristaltic or rotary vacuum pump, is located in the boat, isolated from the sampling jar; (4) the sampling jar can be continuously flushed with sample, at sampling depth, to equilibrate the system; and (5) the sample does not travel through long lengths of tubing that are more difficult to clean and keep clean [1003]. In addition, the device is designed to eliminate atmospheric contact with the sample during collection [1003].

Selection of a representative site for surface water sampling is based on many factors including: study objectives, water use, point source discharges, non-point source discharges, tributaries, changes in stream characteristics, types of stream bed, stream depth, turbulence, and the presence of structures (bridges, dams, etc.) [1003]. When collecting samples to determine ambient levels of trace metals, the presence of potential sources of metal contamination are of extreme importance in site selection [1003].

Ideally, the selected sampling site will exhibit a high degree of cross-sectional homogeneity [1003]. It may be possible to use previously collected data to identify locations for samples that are well mixed or are vertically or horizontally stratified [1003]. Since mixing is principally governed by turbulence and water velocity, the selection of a site immediately downstream of a riffle area will ensure good vertical mixing [1003]. Horizontal mixing occurs in constrictions in the channel [1003]. In the absence of turbulent areas, the selection of a site that is clear of immediate point sources, such as industrial effluents, is preferred for the collection of ambient water samples) [1003].

To minimize contamination from trace metals in the atmosphere, ambient water samples should be collected from sites that are as far as possible (e.g., at least several hundred feet) from any metal supports, bridges, wires or poles [1003]. Similarly, samples should be collected as far as possible from regularly or heavily traveled roads [1003]. If it is not possible to avoid collection near roadways, it is advisable to study traffic patterns and plan sampling events during lowest traffic flow [1003].

The sampling activity should be planned to collect samples known or suspected to contain the lowest concentrations of trace metals first, finishing with the samples known or suspected to contain the highest concentrations [1003]. For example, if samples are collected from a flowing river or stream near an industrial or municipal discharge, the upstream sample should be collected first, the downstream sample collected second, and the sample nearest the discharge collected last [1003]. If the concentrations of pollutants is not known and cannot be estimated, it is necessary to use precleaned sampling equipment at each sampling location [1003].

One grab sampler consists of a heavy fluoropolymer collar fastened to the end of a 2-m-long polyethylene pole, which serves to remove the sampling personnel from the immediate vicinity of the sampling point [1003]. The collar holds the sample bottle [1003]. A fluoropolymer closing mechanism, threaded onto the bottle, enables the sampler to open and close the bottle under water, thereby avoiding surface microlayer contamination [1003]. Polyethylene, polycarbonate, and polypropylene are also acceptable construction materials unless mercury is a target analyte [1003]. Assembly of the cleaned sampling device is as follows:

Sample collection procedure—Before collecting ambient water samples, consideration should be given to the type of sample to be collected, the amount of sample needed, and the devices to be used (grab, surface, or subsurface samplers) [1003]. Sufficient sample volume should be collected to allow for necessary quality control analyses, such as matrix spike/ matrix spike duplicate analyses [1003].

It is recommended that 1 mL of ultrapure nitric acid be added to each vial prior to transport to the field to simplify field handling activities [1003].

Preservation of aliquots for metals other than trivalent and hexavalent chromium—Using a disposable, precleaned, plastic pipet, add 5 mL of a 10% solution of ultrapure nitric acid in reagent water per liter of sample [1003]. This will be sufficient to preserve a neutral sample to pH <2 [1003].

Other Methods:

One 1987 reference stated that polarography is most effectually suitable to the determination of chromium (VI) compounds. Chromium (VI) is electrochemically active over the entire pH range, so that medium pH can be selected for measuring, thus protecting samples most effectively from undergoing redox reactions during the analytical procedure. In some cases sample pre-treatment can be employed to eliminate reductants prior to final measurement (Harzdorf AC; Int J Environ Anal Chem 29, 4,: 249-61 (1987)[609].

Many labs simply analyze residues for total chromium rather than trying to separate chromium 3 and 6. The following information relates to total chromium:

Determination of chromium has often been by an atomic absorption technique using either direct aspiration into a flame or a furnace [893].

Many methods have been used to monitor for chromium [861,927]. Low concentration criteria or benchmarks may require relatively rigorous methods, while routine applications may require only inductively coupled plasma (ICP) analyses. Detection limits should be no higher than comparison benchmarks or criteria for various media (water, sediments, soil, tissues, etc), some of which are low (see sections above). Otherwise, the detection limits should usually not exceed the following default concentrations often recommended by the Fish and Wildlife Service and the National Park Service: Total chromium detection limits of 0.50 ppm dry weight in tissues, 1.0 ppm in sediments and soils, 0.003 ppm (mg/L) in water (Roy Irwin, National Park Service, Personal Communication, 1996).

EPA 1996 IRIS information for drinking water [893]:

Monitoring Requirements

Ground water systems monitored every 3 years; surface water systems monitored annually; systems out of compliance must begin monitoring quarterly until system is reliably and consistently below MCL.

Analytical Methods

Atomic absorption/furnace technique (EPA 218.2; SM 304); inductively coupled plasma (EPA 200.7): PQL= 0.01 mg/L.

See also: Chromium entry.