

ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

CHROMIUM (IN GENERAL) 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 data from 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 uninformed 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:

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on the internet or NTIS: 1998).

## Chromium, General (Cr, CAS number 7440-47-3)

NOTE: This entry contains mostly information on elemental chromium and chromium in general, although some information on chromium III and chromium VI is also included. For specific information on these two ionic forms, see the entries entitled Chromium III and Chromium VI.

### **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 is also listed among the 25 hazardous substances thought to pose the most significant potential threat to human health at priority superfund sites [93]. Chromium received special attention in studies of subsurface agricultural irrigation drainage waters of the San Joaquin Valley of California because it was determined to be a "substance of definite concern" [445].

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]. 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].

Most compounds prepared from chromite ore (that is, aggregate of minerals from which chromium compounds can be extracted) contain chromium in the more stable +3 state. The chromium in essentially all environmentally important compounds is in one of these two oxidation states [24]. Trivalent chromium is the most common form in rocks of the earth's crust, but both trivalent and hexavalent chromium occur as dissolved chromium [190].

Chromium compounds are stable in the trivalent state and occur in nature in this state in ores, such as ferrochromite (FeCr<sub>2</sub>O<sub>4</sub>). The hexavalent state is the second most stable state. However, hexavalent chromium rarely occurs naturally, but is produced from anthropogenic sources [927]. Most of the chromium (+6) found in nature is a result of domestic and industrial emissions. Interaction of +6 chromic oxide, dichromate, or chromate compounds with organic compounds can result

in reduction to the comparatively less toxic trivalent form [24]. Hexavalent chromium occurs naturally in the rare mineral crocoite [927].

**Br.Haz:** General Hazard/Toxicity Summary:

NOTE: The potential hazards and benefits of chromium are complex, so the below summary is divided into several sections: Potential Hazards of Chromium in General, Potential Benefits of Chromium in General, Potential Hazards of Chromium VI, and Potential Hazards of Chromium III.

Potential Hazards of Chromium in General:

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 often (not always) have a lower order of toxicity or biological hazard [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) [940].

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 (Cr<sup>6+</sup>, 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]. 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]. For many metals, alkalinity is sometimes a more important co-factor for toxicity than hardness (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

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 [940]. 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 general population is exposed to chromium by eating food, drinking water, and inhaling air that contain chromium [927]. The carcinogenic risk and oxidizing agent hazard from hexavalent (chromium +6) compounds, 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].

EPA has a free health advisory on this metal, available through the Office of Drinking Water, EPA, Washington, D.C. or through NTIS. Several comprehensive reports on the hazards of chromium, including Cr+3 and Cr+6, are available. Chromium hazards to fish and wildlife were summarized in Eisler's 1986 synoptic review [24]. More recently, Environment Canada has prepared a priority substances list assessment report for chromium [926]. ATSDR has prepared a toxicological profile for chromium which summarizes human health effects via various exposure routes [927], most of which has not yet been summarized herein due to lack of time.

#### Potential Benefits of Chromium in General:

Trace quantities of certain forms of chromium are considered helpful or necessary [366,483]. Chromium supplement pills are even sold in some health food stores. Chromium in biological materials is usually in the +3 form, and is the form that functions as an essential element in mammals by maintaining efficient glucose, lipid, and protein metabolism [24].

Chromium appears to play an important role in the maintenance of vascular integrity. A deficiency of this metal in animals results in elevated serum cholesterol levels and increased atherosclerotic aortic plaques. Autopsies of humans have revealed

virtually no chromium in the aortas of individuals dying of atherosclerotic heart disease, in comparison with normal individuals dying of other causes [494,940].

In humans and animals, chromium (III) is an essential nutrient that plays a role in glucose, fat, and protein metabolism by potentiating the action of insulin [927]. The biologically active form of chromium, called glucose tolerance factor (GTF), is a complex of chromium, nicotinic acid, and possibly amino acids (glycine, cysteine, and glutamic acid) [927]. Both humans and animals are capable of converting inactive inorganic chromium (III) compounds to physiologically active forms [927].

Misc. excerpts of information on potential benefits of chromium from the HSDB [940]:

Chromium is an essential nutrient for man, being required for the maintenance of normal glucose tolerance.

Chromium assists in binding insulin to fat cell membranes stimulating them to absorb glucose. ...

Trypsin contains chromium as an integral part. ...

Deficiency of chromium in the diet of animals causes a syndrome simulating diabetes. ...

A lack of chromium has been associated with atherosclerotic heart disease, elevated cholesterol levels in the blood, and high fat content of the aorta. ...

Chromium is essential for sugar and fat metabolism. ...

Corneal lesions have been observed in rats deficient in both chromium and protein; no lesions have been seen with either single deficiency. ...

Impairment of glucose tolerance is the first response of animals to a mild chromium deficiency. A more severe deficiency can be produced by raising animals in an environment that allows strict control of airborne contamination or by subjecting them to additional stress, such as low-protein diets,

hemorrhage or strenuous exercise. ...

Chromium deficiency in rats resulted in significantly increased concentrations of circulating cholesterol and incidences of aortic plaques. ...

Some disorders caused by lack of manganese can be treated with chromium (Cr). ...

Chromium (Cr) supplemented animal diets reduced incidence of atherosclerosis. ...

Protein-calorie malnutrition and the syndrome of kwashiorkor and marasmus improve when children are fed one dose of 250 ug Cr. ...

A chromium supplements such as Brewer's yeast extract can have beneficial effects in some cases, particularly with the elderly, malnourished children, and diabetics. ...

#### Potential Hazards of Chromium VI:

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 (many strong 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<sup>6+</sup>) 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].

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, osmoregulatory upset, alterations in population structure and species diversity indices, and inhibition of photosynthesis [24].

#### Potential Benefits of Chromium III:

Small amounts of trivalent chromium are considered essential in animals and man [366]. Trivalent chromium (Cr<sup>3+</sup>) is an essential human and animal nutrient at levels of 50 to 200 micrograms/day [929].

Trivalent chromium is the only form of chromium known to play a beneficial biological role. The form must be supplied as a stable complex, as trivalent chromium exists as an insoluble (sic, actually "relatively insoluble") macro-molecule at normal blood pH. The known biological effect of trivalent chromium is the maintenance of normal glucose tolerance [445].

Trivalent chromium (Cr<sup>3+</sup>, chromium +3) is an essential element for fungi and vertebrates in general [366,483,940]. Trivalent chromium is considered essential for glucose and lipid metabolism in mammals, and a deficiency of it produces symptoms of diabetes mellitus [483,940]. Trivalent chromium is essential for the maintenance of normal glucose tolerance in animals and man, and the factor or the group of factors containing trivalent chromium, called GTF (glucose tolerance factor) has been suggested to be responsible for this favorable action of chromium [366].

Chromium(III) may stabilize biological proteins in their proper configurations. /Cr(III)/ (Mertz W; *Physiol Rev* 49: 165-239, 1969, as cited in Nat'l Research Council Canada; *Effects of Chromium in the*

Canadian Envir p.67 (1976) NRCC No.15017) [940].

Trivalent chromium is essential in mammals. Adequate trivalent chromium nutrition improves growth and longevity and, along with insulin, helps to maintain correct glucose, lipid, and protein metabolism. /Trivalent chromium/ (Nat'l Research Council Canada; Effects of Chromium in the Canadian Environment p.94, 1976, NRCC No 15017) [940].

Studies with mammals have suggested that trivalent chromium is not well absorbed from the intestinal tract. For example, rat studies have indicated that only a few percent of an oral chromium+3 dose crosses the intestinal wall, regardless of previous dietary history. However in studies of small intestinal absorption in black ducks (*Anas rubripes*), Eastin et al. (1980) measured equal rates of absorption of trivalent chromium (as chromium potassium sulfate [ $\text{CrK}(\text{SO}_4)_2$ ]) and hexavalent chromium (as chromium trioxide [ $\text{CrO}_3$ ]). They noted that the ionic form of chromium influenced the degree of its absorption, with anionic chromium complexes being better absorbed [445].

#### Potential Hazards of Chromium III:

Although chromium (III) is an essential nutrient, exposure to high levels via inhalation, ingestion, or dermal contact may cause some health effects [927]. In general, the toxicity of trivalent chromium to mammals is low because membrane permeability is poor and it is noncorrosive [24]. However, chromium deficiency is unknown, and too much chromium can be harmful to humans [173]. Also, sensitivity to chromium varies widely, even among closely related species (that is, biota) [24].

Since the valence states are subject to change, tissues are often analyzed for total chromium rather than only chromium III or VI. During the laboratory digestion of tissue samples, most chromium is changed to the trivalent form.

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 be 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].

Because trivalent chromium in natural waters is frequently found in particulate form, ingestion is a common route of exposure in aquatic species [445].

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

Total Chromium and Chromium in General:

Like Chromium VI (CAS 18540-29-9), Chromium in general (CAS 7440-47-3) is listed by EPA as a class A human carcinogen. This basically means there is decisive evidence of carcinogenicity in humans [952].

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

Under appropriate conditions, Cr is a human and animal carcinogenic agent; its biological effects depend on chemical form, solubility and valence [24]. However most references concentrate on Chromium VI as the most carcinogenic form.

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]. There is little consistent convincing evidence of associations between exposure to trivalent chromium and cancer [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].

#### Chromium VI (Hexavalent Chromium):

Chromium VI is listed by EPA as a class A human carcinogen (basically means there is decisive evidence of carcinogenicity in humans [893].

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].

The steps in the mechanism of cancer induction of Cr6+ [929]:

- (1) Only certain Cr6+ compounds have the capacity to interact with cellular components;
- (2) Cr6+ is reduced by body fluids and excess Cr6+ enters the cell (Cr3+ is poorly absorbed across membranes);
- (3) cellular organelles and the cytoplasm reduce Cr6+ to Cr3+;
- (4) excess Cr6+ can enter the nucleus;
- (5) Cr6+ reduction through 5+ and 4+ to 3+ has a potential to interact with the DNA molecule; and
- (6) if unrepaired, this DNA damage can lead to cancer induction [929]. On the basis of current evidence Cr6+ has a threshold for carcinogenic

potential in humans that is greater than the current TLV [929].

Chromium III (Trivalent Chromium):

Classification of carcinogenicity for trivalent chromium: 1) evidence in humans: inadequate; 2) evidence in animals: inadequate. Overall summary evaluation of carcinogenic risk to humans is group 3: The chemical is not classifiable as to its carcinogenicity to humans. /From table, trivalent chromium compd/ (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. S7 60, 1987) [609].

Experiments in mice, rats, hamsters, guinea pigs and rabbits to investigate the carcinogenicity of chromic(III) acetate, chromic(III) oxide ... Chromium (VI) trioxide, chromium metal ... Sodium chromate (VI) ... Sodium dichromate (VI) ... Chromium(III) sulfate ... Were inadequate to evaluate the carcinogenicity of these chromium compounds (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 302, 1980) [609].

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

At high environmental concentrations, chromium is a mutagen, teratogen, and carcinogen [24]. 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]. While a variety of genetic effects have been induced by trivalent chromium in subcellular or acellular systems, in general, trivalent compounds have not been genotoxic in cultured animal or human cells [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].

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].

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]. There is no reliable information that any form of chromium has harmful effects on reproduction or causes birth defects in humans [927].

Chromium rapidly accumulates in the testes and then in the epididymes after injection of a tracer dose, thus suggests a possible incorporation of chromium into sperm [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; Zancchi 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:

Although the most important valences of chromium are 3 and 6, chromium with valences of 1, 2, 4, and 5 has also been shown to exist in a number of compounds [343].

Depending on the physical and chemical state of the chromium, the same elemental concentration has a wide variety of mobilities and reactivities and thus has difference effects [24]. Chromium toxicity to aquatic

biota is significantly influenced by abiotic variables such as hardness, temperature, pH, and salinity of water [24]. In both freshwater and marine environments, hydrolysis and precipitation are the most important processes that determine the fate and effects of chromium, whereas adsorption and bioaccumulation are relatively minor [24]. Both Cr<sup>+3</sup> and Cr<sup>+6</sup> can exist in water with little organic matter; Cr<sup>+6</sup> is usually the major species in seawater. Under oxygenated conditions, Cr<sup>+6</sup> is the dominant dissolved stable Cr species in aquatic systems [24].

A very small amount of the chromium in soil, however, will dissolve in water and can move deeper in the soil to underground water [927]. The movement of chromium in soil depends on the type and condition of the soil and other environmental factors [927]. Trivalent chromium compounds, except for acetate, nitrate, and chromium (III) chloride-hexahydrate salts, are generally insoluble in water [927]. Some hexavalent compounds, such as chromium trioxide (or chromic acid) and the ammonium and alkali metal (e.g., sodium, potassium) salts of chromic acid are readily soluble in water [927]. The alkaline metal (e.g., calcium, strontium) salts of chromic acid are less soluble in water [927]. The zinc and lead salts of chromic acid are virtually insoluble in cold water [927]. Chromium (VI) compounds are reduced to chromium (III) in the presence of oxidizable organic matter [927]. However, in natural waters where there is a low concentration of reducing materials, chromium (VI) compounds are more stable (EPA 1984a) [927]. For more information on dissolved vs. total vs. acid soluble chromium, see Laboratory section far below.

Chromium in water may originate from surface runoff, deposition from air, or release of wastewaters [445]. Chromium may be transported in waters as suspended materials and deposited in estuaries and bays but it is more frequently removed from water by sedimentation [445]. 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].

There is little tendency for chromium (+3) to biomagnify in food chains in the inorganic form. However, organo-trivalent chromium compounds may have significantly difference accumulation tendencies although little is know about these compounds [24].

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 [366].

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 adsorption and precipitation reactions, and can thus remain in the water column [926].

Although there are few oxidants capable of converting Cr+3 to 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<sub>2</sub>O<sub>2</sub> 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].

Hexavalent chromium, the form used in chrome plating, tends to be more soluble and thus moves around in the

environment more than trivalent chromium. Because of its higher solubility, hexavalent chromium is considered more mobile than trivalent chromium in aquatic ecosystems [445].

Highway runoff routed through a detention pond and then a cypress wetland resulted in much higher sediment levels in the detention pond than in the wetland [220]. However, the same study indicated that chromium deposits in a freshwater wetland were not always nearest the inlet, possibly indicating that chromium travels farther before settling or adsorbing than some other metals [220].

One strategy for remediating 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].

Movement of chromium in the soil profile is dependent on several variables, including, pH, oxidation state, soil minerals, and the presence of ions or other compounds that may compete or bind with chromium [445]. Hexavalent chromium in soil is easily converted to trivalent chromium by the presence of organic matter, even at alkaline pH (Bartlett and Kimble, 1976). Hexavalent chromium tends to move downward in the soil column with increasing pH while trivalent chromium is more adsorbed as pH increases [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].

In humans, Cr6+ is reduced by body fluids and excess Cr6+ enters the cell (Cr3+ is poorly absorbed across membranes) [929]. Cellular organelles and the cytoplasm reduce Cr6+ to Cr3+ [929]. Excess Cr6+ can enter the nucleus [929]. Cr6+ reduction through 5+ and 4+ to 3+ has a potential to interact with the DNA molecule. If unrepaired, this DNA damage can lead to cancer induction [929].

Airborne chromium exists naturally in particulate matter as a result of geochemical processes and can be found in either hexavalent or trivalent forms [445]. Sea salt is not believed to add significantly to chromium concentrations found in aerosols [445].

**Synonyms/Substance Identification:**

CHROM (GERMAN) [609]  
CHROME [609,617]  
CHROME (FRENCH) [609]  
Chromium metal [617]

Molecular Formula [609,617]:  
Cr

**Associated Chemicals or Topics (Includes Transformation Products):**

See also individual entries:

Chromium III  
Chromium VI

In plants, chromium (Cr) interferes with uptake translocation, and accumulation by plant tops of calcium, potassium, magnesium, phosphorus, boron, copper (see interactions section below for details).

**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):

Only 11 of 720 surface water values exceeded 5 ug/L [190].

Concentration of total Cr in contaminated surface waters in Alberta, Canada, ranged from 1 to 55 ug/L, and averaged 5.1 ug/L [926].

**W.Typical** (Water Concentrations Considered Typical):

USGS 1985: 10 ug/L [190].

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

California, 1986: Ambient background level for water concentrations of chromium +3 was 5 ug/l [222].

Typical Ocean Concentrations: EPA 1981: 0.00005 mg/l [83]. In ocean water, the mean chromium concentration is 0.3 ug/L (1982) [927].

Typical Freshwater Concentrations: EPA 1981: 0.00018

mg/l [83].

USGS 1985: 5.8 ug/l typical for North American Rivers [190].

The chromium concentrations in U.S. river waters usually range from 1 to 30 ug/L, with a median value of 10 ug/L [927]. The total chromium concentrations in 1978 in U.S. drinking waters range from 0.4 to 8.0 ug/L, with a mean value of 1.8 ug/L [927]. Some of the older chromium concentrations are suspect due to methodology issues [927]. Chromium concentrations in drinking water [mostly as chromium(III)] are generally very low, less than 2 parts of chromium in a billion parts of water (2 ppb) [927].

USGS 1974-1981: the 50th percentile of 161 (not especially clean) NASQWAN and NWQSS river sites in the U.S. was 10 ug/l; the 25th percentile was 9 ug/l, and the 75th percentile was 10 ug/l, with concentrations trending upward more often than downward [219]. These riverine sites in the USGS study were mostly in (or downstream of) agricultural and urban areas [219].

Median Concentration for Public Water Supplies: 0.43 ug/L [190].

Average Concentration for River Waters: 1.4 ug/L [190].

Average Concentration in Rivers and Lakes: 1 - 10 ug/L [24].

Drinking water: usually < 8, rarely > 50 [24].

Median concentration of chromium in two surveys of drinking water supplies in 70 and 71 sites across Canada in 1976 and 1977, respectively, were  $\leq$  2.0 ug/L [926].

Average concentrations of total chromium (including Cr+3 and Cr+6 in dissolved and particulate phases) in uncontaminated surface and marine waters are generally below 1 ug/L [926].

In a survey of 1,577 surface waters within the continental United States, chromium was found in 24.5% of the samples with a range of 1-112 ppb (mean = 9.7 ppb) [445]. Chromium concentrations in waters of the San Luis Drain and Kesterson Reservoir were 4-50 ug/l (ppb) and <1-19 ug/l, respectively [445]. Seawater generally contains less chromium than freshwater (0-0.5 ppb); however, it contains a more significant proportion of hexavalent than trivalent chromium [445]. In freshwaters with little organic matter, both forms of chromium may exist [445].

**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):

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 discussion, see the Laboratory and/or Field Analyses section (far below) and USEPA 1984 Ambient Water Quality Criteria Document for Chromium.

NOTE: See also entries entitled Chromium III and Chromium VI for specific information. There are no 1996 national water quality criteria for total chromium but there are criteria and benchmarks for Chromium III and Chromium VI [893].

Florida's water quality standard applied to some wetland sites was 50 ug/l [220].

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 State of California has established no water quality objectives for chromium, for the protection of fish and wildlife in the San Joaquin Valley. Additionally, no regulatory standards currently exist for the protection of fish and wildlife from dietary exposure to chromium.

The U.S. Environmental Protection Agency has established two sets of freshwater aquatic life water quality criteria for chromium, one set each for chromium+3 and chromium +6. The water quality criteria for chromium+6 are: chronic = 11 ug/l (ppb) and acute = 16 ug/l (See Chromium VI entry).

Water quality criteria (in ug/l) for chromium+3 are water hardness dependent and can be determined using the following formulae [445,649]:

$$\text{chronic} = e(0.8190[\ln(\text{hardness})]+1.561)$$

$$\text{acute} = e(0.8190[\ln(\text{hardness})]+3.688).$$

Further clarification:

e is the base of natural logarithms and numerically equals 2.72 (rounded), and  $\ln(\text{hardness})$  equals the natural logarithm of the measured hardness (Gary Rosenlieb, National Park Service, Personal Communication, 1997).

Although current criteria for environmental concentrations of chromium are set separately for trivalent and hexavalent chromium, because of possible chemical interconversions in natural waters, it has been recommended that water quality standards be set for total chromium concentrations [445]. See also: entries for Chromium III and Chromium VI.

**W.Plants (Water Concentrations vs. Plants):**

Shallow Groundwater Ecological Risk Assessment Screening Benchmark for Terrestrial Plants Listed by Oak Ridge National Lab, 1994 [651]:

To be considered unlikely to represent an ecological risk, field concentrations in shallow groundwater or porewater should be below the following benchmark for any aqueous solution in contact with terrestrial plants. Toxicity of groundwater to plants may be affected by many variables (pH, Eh, cation exchange capacity, moisture content, organic content of soil, clay content of soil, differing sensitivities of various plants, and various other factors). Thus, the following solution benchmark is a rough screening benchmark only, and site specific tests would be necessary to develop a more rigorous benchmark for various combinations of specific soils and plant species [651]:

For CAS 7440-47-3, Chromium, the

benchmark is 0.05 mg/L (groundwater or porewater).

**W. Invertebrates (Water Concentrations vs. Invertebrates):**

Information from Moore [445]:

Reader caution: There may be some electronic transmission errors in the following (indented) text from Moore, so refer to the original hardcopy text for confirmation for use in critical applications and for documentation of the references in parentheses). This information provided with permission of senior author Stephen Moore for the sole purpose of preliminary information searching convenience [445]:

The acute toxicity of waterborne hexavalent chromium in freshwater species has been reported to range from 23.07 ppb (a cladoceran) to 1,870,000 ppb (a stonefly) (USEPA, 1986).

A rotifer (*Philodina acuticornis*) was used as a test organism to estimate the toxicity of chromium and other heavy metals to fish and other aquatic organisms (Buikema et al., 1974). Rotifers are an important part of the aquatic food chain. The EC50 (the estimated concentration of toxicant that caused 50% of test organisms to stop moving when exposed to bright light) for chromium+6 (as potassium dichromate [K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>]) was 42.0, 50.0, and 3.1 ppm in soft water (25 ppm added calcium sulfate [CaSO<sub>4</sub>], calcium carbonate [CaCO<sub>3</sub>], and magnesium sulfate [MgSO<sub>4</sub>]) at 24-, 48-, and 96-hours, respectively. In moderately hard water (81 ppm of the same added chemicals noted above) those same data points were 23.0, 19.0, and 15.0 ppm chromium, respectively. Thus, toxicity of chromium to the rotifer was increased by an increase in water hardness at 24- and 48-hours of exposure, but decreased at 96-hours. pH of test waters was 7.4-7.8.

The EC50 for daphnia exposed to waterborne hexavalent chromium was determined by Khangarot and Ray (1987). Water chemistry in these studies included hardness of 240 ppm (as calcium carbonate) and pH of 7.4-7.8. The 24-hour EC50 was 2.2 ppm and the 48-hour EC50 was 1.79 ppm. Toxicity to daphnia was not

significantly different between 24- and 48-hours of exposure, suggesting that cumulative toxicity did not occur.

The acute toxicity of chromium+3 to several species of benthic organisms was determined by Rehwoldt et al. (1973). Species common to the Hudson River were exposed to varying concentrations of trivalent chromium in water of pH 7.6 and hardness of 50 ppm. The 24-hour median tolerance limits (TLM's) for bristle worm, scud, caddisfly, damselfly, midge, snail eggs, and adult snails exposed to chromium+3 were found to be 12.1, 6.4, 58, 46, 16.5, 15.2, and 10.2 ppm, respectively. Ninety-six hour TLM's were reported as 9.3, 3.2, 50, 43.1, 11.0, 12.4, and 8.4 ppm chromium+3 for the same organisms, respectively.

The acute toxicity of hexavalent chromium (as potassium dichromate) to the freshwater prawn (*Macrobrachium lamarrei*) was studied by Murti et al. (1983). Water chemistry in these studies included hardness of ~111 ppm (as calcium carbonate) and pH of ~7.4. LC50 values for 24-, 48-, 72-, and 96-hours of waterborne chromium+6 exposure to prawns were 5.44, 3.69, 2.47, and 1.84 ppm, respectively. Carbohydrate metabolism also was disturbed, as evidenced by changes in hemolymph glucose levels.

Temperature and salinity have been found to affect the acute toxicity of chromium to estuarine invertebrates; high temperature and low salinity causing the greatest toxicity. Chromium and other metal toxicities to *Corophium volutator*, *Macoma balthica*, and *Nereis diversicolor* were found to vary over 2 orders of magnitude, depending on these conditions (McLusky and Bryant, 1985).

#### **W.Fish (Water Concentrations vs. Fish):**

Information from Moore [445]:

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permission of senior author Stephen Moore for the sole purpose of preliminary information searching convenience [445]:

The value for pH was found to affect uptake, tissue distribution and retention, and toxicity of chromium+6 (as sodium chromate [Na<sub>2</sub>CrO<sub>4</sub>]) in yearling and fingerling rainbow trout (*Salmo gairdneri*) (van der Putte et al., 1981b). In short-term (2 or 4 day) experiments, fish were exposed to varying concentrations (2.0-40 ppm) of waterborne chromium+6 at either pH 6.5 or 7.8, and 80 ppm hardness (as calcium carbonate), to determine the effect on the above variables. At pH 7.8, uptake of chromium was rapid in fingerling trout and tended to accumulate in internal organs rather than gills, as was the case in fish at pH 6.5. Equilibrium did not appear to occur in gill tissues of trout at pH 6.5; accumulation of chromium continued to increase during the exposure period. Mortality was greater in trout at pH 6.5, which may have reflected differences in chromium uptake from the gill. Chromium elimination rate, following removal from chromium exposure, was higher in fish kept at pH 6.5.

The value for pH also was found to affect the acute toxicity of waterborne hexavalent chromium (as sodium chromate) to different size rainbow trout, with toxicity increasing as pH decreased (van der Putte et al., 1981a). Water hardness in these studies was 77.5-82.5 ppm (as calcium carbonate). Toxicity (determined as the LC<sub>50</sub>) was approximately 2-4 times greater when trout were in a pH 6.5 versus a pH 7.8 environment. Toxicity of hexavalent chromium also was found to be greater in younger trout and following a longer duration of exposure.

Immune responses of fish may be affected by short-term exposure to waterborne hexavalent chromium (Sugatt, 1980). Juvenile coho salmon (*Oncorhynchus kisutch*) were inoculated with one of several dilutions of *Vibrio anguillarum* (a bacterial pathogen) and exposed to a sublethal concentration of chromium+6 (0.5 ppm as sodium dichromate [Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>]) for 2 weeks. Water chemistry in these studies included hardness of 56-60 ppm (as calcium carbonate) and pH of 6.6-7.3. Disease resistance (with mortality as an endpoint) and acquired immune

response (measured by agglutinin production) were significantly impaired by chromium+6 exposure compared to controls.

A number of biochemical indices associated with carbohydrate metabolism are altered in *Channa punctatus* (a freshwater murrel, aka the snakehead fish) by chronic exposure to sublethal concentrations of waterborne hexavalent chromium (Sastry and Sunita, 1983; 1982; Sastry and Tyagi, 1982). The authors speculated that accumulation of chromium+6 in liver, kidney, and gills may damage these tissues with resultant negative effects on fish metabolism (Sastry and Sunita, 1983).

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 ppt) water (pH 7.9).

The effect of waterborne chromium (as  $\text{Cr}_2(\text{SO}_4)_3$  [Merck]) on fertilization in rainbow trout was evaluated by Billard and Roubaud (1985). Chromium had a cytotoxic effect on spermatozoa at concentrations less than 5 ppb; however, concentrations up to 1 ppm did not affect ova in separate tests. When the ova and spermatozoa were mixed together and insemination carried out (which measured sperm motility as well as cytotoxicity), the toxicity level for chromium was also less than 5 ppb. pH in these tests was 9.0.

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 of waterborne trivalent chromium to rainbow trout fry was determined to be 11.2 ppm by Bills et al. (1977). Previous exposure to low and high concentrations of the polychlorinated biphenyl, Aroclor 1254, decreased the LC50 values of chromium+3 to 9.0 and 7.05 ppm, respectively.

Creek water from a mining region of South Dakota was used to determine the toxicity of mining wastes (Hale, 1977). Two-month old rainbow trout were placed in creek water (pH 6.4-8.3) with added gradients of chromium+3 (as chromium nitrate [Cr(NO3)3]). The 96-hour TL50 was estimated to be 24.09 ppm for waterborne trivalent chromium.

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.

Results of these studies indicated that growth rates were depressed (20-30%) in brook trout and rainbow trout at all concentrations tested during 8-months of exposure. Growth effects were somewhat temporary and brook trout exposed to chromium+6 weighed only 10-12% less than controls after 12-22 months. Rainbow trout exposed to 0.34 ppm chromium+6 or greater and brook trout exposed to 0.76 ppm chromium+6 or greater, died after 3 months on test. Spawning success was very high (99%) in brook trout at the lowest concentration of chromium+6 (0.35 ppm); however, survivability after 3 months at this concentration was 22% less than controls and surviving fish were smaller. The authors concluded that the MATC is between 0.20 and 0.35 ppm hexavalent chromium for brook and rainbow trout in soft water.

Arillo et al. (1982) studied adult rainbow trout exposed to 200 ppb waterborne hexavalent chromium (as potassium dichromate) for 3 months. Water chemistry in this study included hardness of 320 ppm (as calcium carbonate) and pH of 7.4. Adult males had a lower hepatic glucide content than controls ( $p < 0.05$ ), while female adult trout were not different from controls in this variable. This effect remained in males after a 3-month recovery period. Male rainbow trout exposed to 200 ppb chromium+6 also experienced increased liver proteolytic activity after 6 months; female trout were not similarly affected by treatment. The authors speculated that these biochemical changes may reflect

serious pathological processes.

Stevens and Chapman (1984) conducted early life stage toxicity tests on steelhead trout (*Salmo gairdneri*) in soft water (~25 ppm calcium carbonate) of pH 5.45-7.20. Newly fertilized eggs were exposed to 10 concentrations of waterborne trivalent chromium (as chromium nitrate) for 72 days. A concurrent test was run with steelhead exposed to 5 concentrations of waterborne chromium+3 for 58 days from the eyed stage to feeding fry. In those fish exposed as fertilized eggs, complete mortality occurred at the highest chromium concentration of 495 ppb; near complete mortality (98%) occurred at the second highest concentration of 271 ppb chromium+3. Sixty-one percent mortality was experienced at a chromium+3 concentration of 157 ppb and 15% mortality ( $p < 0.05$ ) occurred at 89 ppb chromium+3. Most of the fish died at hatching and a significant proportion of those were unable to break the chorion. Hatching was delayed approximately 24 hours in all chromium+3 concentrations. For those fish begun at the eyed stage, chromium+3 tolerance was greater compared to those begun at fertilization; a significant decrease in survivability (75%) did not occur until chromium+3 concentrations reached 271 ppb. These differences may have been the result of the duration of exposure. The authors determined the chronic toxicity threshold to lie between 30 ppb chromium+3 (no apparent effect) and 157 ppb chromium+3 (unacceptable toxic effect).

Stevens and Chapman (1984) also determined the 96-hour LC50 of waterborne chromium+3 (as chromium nitrate) for steelhead trout juveniles surviving the early-life-stage chronic toxicity test. Juveniles surviving control treatments and the 6 concentrations of waterborne chromium (13-157 ppb chromium+3) in the chronic test were used in a 96-hour acute toxicity test to determine whether acclimation to chromium occurred. Fish were exposed to 5 concentrations of chromium+3 (2,125-12,200 ppb). The test indicated that prior exposure to chromium did not increase the tolerance of these fish to acutely toxic doses of chromium+3. Fish that had been previously exposed to 48 and 89 ppb chromium+3 tended to be less tolerant than those previously exposed

to lower concentrations of chromium.

Stevens and Chapman (1984) also conducted a standard 96-hour LC50 for juvenile steelhead trout exposed to chromium+3 (as chromium nitrate). Eight concentrations of waterborne chromium (1,100-5,825 ppb) and 2 controls were tested. Water chemistry in these studies included hardness of 25 ppm (as calcium carbonate) and pH of 7.4. The standard 96-hour LC50 for juvenile steelhead trout was determined to be 4,400 ppb chromium+3.

The USFWS-NFCRC (Dec 1987) conducted two sets of experiments to determine the 24- and 96-hour LC50's for fall-run chinook salmon (*Oncorhynchus tshawytscha*) exposed to waterborne hexavalent chromium (as sodium dichromate). Test water was standardized to simulate the cation and anion concentrations of San Luis Drain water (without the trace elements) and was then diluted with either freshwater or brackish water. In the first tests, the salmon's swimup life stage (0.5 g) was exposed to chromium+6 and simulated drain water diluted 10-fold with freshwater. Water hardness in those tests was 211 ppm (as calcium carbonate) and pH was 7.9. In the second tests, the salmon's advanced fry life stage (2 g) was exposed to chromium+6 and drain water diluted 10-fold with brackish water (salinity ~1.2 ppt). Water hardness in those tests was 347 ppm (as calcium carbonate) and pH was 7.8. The 24- and 96-hour LC50 values for the swimup-life-stage salmon were 261 and 111 ppm, respectively. The same values for the larger salmon were 310 and 144 ppm, respectively. The LC50's did not differ between the two water quality tests.

Sauter et al. (Oct 1976) attempted to assess the "no effect" concentration of waterborne hexavalent chromium (as sodium dichromate) to eggs and fry of 7 species of fish in soft water (30-46 ppm calcium carbonate) of pH 6.7-7.4. Rainbow trout were exposed to chromium in 2 separate experiments. In the first, concentrations ranged from 1.6-49.7 ppm chromium+6 and in the second, chromium+6 concentrations ranged from 51-822 ppb chromium. Trout eggs exposed to 26.7 or 49.7 ppm chromium+6 did not hatch and those exposed to 6.1 or 12.2 ppm chromium+6 had significantly lower hatching success than

controls or those trout exposed to lower chromium+6 concentrations. Fry exposed to 12.2 ppm chromium+6 for 30 days did not survive, and 3.2 or 6.1 ppm chromium+6 in water for 30 days caused a significant decrease in survivability of trout fry when compared to controls. All concentrations of chromium+6 in this experiment caused a reduction in total lengths of fry. In days 31-60 of the experiment, the lowest concentration of chromium+6 (1.6 ppm) led to a significant decrease in survival, length, and weight of trout fry. In the second experiment, 822 ppb chromium+6 decreased survival in trout fry over a 60-day period; concentrations of 384 and 822 ppb chromium decreased fry length when compared to controls after 60 days; and concentrations greater than or equal to 105 ppb chromium+6 for 60 days depressed weights of trout fry. The MATC for trout fry under these conditions was estimated to fall between 51 and 105 ppb chromium+6.

Similar experiments were carried out by Sauter et al. (Oct 1976) with lake trout (*Salvelinus namaycush*) eggs and fry. In the first experiment, 6 concentrations of waterborne chromium+6 (1.4-50.7 ppm, as sodium dichromate) were tested; hatching of eggs did not occur following exposure to 50.7 ppm and was significantly lowered after exposure to 24.4 ppm chromium+6. Mortality was complete in trout fry exposed for 30 days to 24.4 ppm chromium+6 or greater. Survival of fry was depressed after 30 days in those fish exposed to 6.0 or 11.6 ppm chromium+6 compared to controls. All chromium+6 concentrations led to decreased fish fry lengths after 30 days of exposure. Although survivability of fry appeared to be reduced following exposure to all chromium+6 concentrations after 60 days, statistically significant differences were only noted at concentrations of 6.0 ppm chromium+6 and above. Lengths and weights of fry were reduced in all chromium+6 concentrations after 60 days.

In the second experiment, lake trout eggs and fry were exposed to lower waterborne chromium+6 concentrations (5 concentrations, 51-822 ppb). Significant adverse effects did not appear to occur following exposure to these concentrations for 30 days; however, fry weights were reduced after 60 days exposure to

194, 394, and 822 ppb chromium+6. The authors estimated the MATC for lake trout exposure to these conditions to fall between 105 and 194 ppb chromium+6.

Channel catfish (*Ictalurus punctatus*) eggs exposed to 6 concentrations of waterborne hexavalent chromium (39-1,290 ppb) had similar hatch percentages, although exposure to chromium+6 concentrations greater than or equal to 305 ppb did cause a decrease in survival and length of fry following 30 days (Sauter et al., Oct 1976). Exposure of catfish to 1,290 ppb chromium+6 for 60 days caused complete mortality; exposure to 570 ppb chromium+6 for 60 days reduced weight, length, and survival of fry. The MATC for channel catfish under these conditions was estimated to fall between 150 and 305 ppb chromium+6.

In a similar experiment with bluegill (*Lepomis macrochirus*) eggs and fry, Sauter et al. (Oct 1976) found that hatching success was not affected by chromium+6 concentrations as high as 1,122 ppb. Likewise, survivability was not affected after 60 days exposure to chromium+6 concentrations from 57 to 1,122 ppb and depression in fish length at higher chromium+6 concentrations did not achieve statistical significance. Bluegill fry weights were significantly reduced following 60 days of exposure to 1,122 ppb chromium+6. The MATC for bluegill under these conditions was estimated to be between 522 and 1,122 ppb chromium+6; however, the authors acknowledged that early feeding difficulties in fry may have concealed growth depression occurring at lower concentrations of chromium+6.

For white sucker (*Catostomus commersoni*) eggs and fry exposed to waterborne chromium+6 (123-1,975 ppb), hatching success was not affected by treatment (Sauter et al., Oct 1976). Survival after 30 or 60 days of chromium+6 exposure was similar among treatments. Length of white sucker fry was reduced following 30 days of exposure to 1,975 ppb chromium+6 compared to controls. Fish length was decreased after exposure to 538, 963, and 1,975 ppb chromium+6 for 60 days. The MATC for white suckers under these conditions was estimated to fall between 290 and 538 ppb chromium+6.

Sauter et al. (Oct 1976) discovered that northern pike (*Esox lucius*) hatching success was not affected by exposure to chromium+6 concentrations from 123 to 1,975 ppb. Survival was decreased; however, in those fry exposed to 963 and 1,975 ppb hexavalent chromium for 20 days. The MATC for northern pike eggs and fry under these conditions was estimated to be between 538 and 963 ppb chromium+6. The authors commented that cannibalism may have masked effects of lower concentrations of chromium+6.

Sauter et al. (Oct 1976) also exposed walleye (*Stizostedion vitreum*) eggs and fry to hexavalent chromium at concentrations of 80-2,167 ppb. These concentrations had no effect on hatching success or survivability after 30 days exposure, although survival was low in all treatment groups and controls because of poor feeding success. The MATC for walleye eggs and fry was estimated at greater than 2,161 ppb hexavalent chromium.

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

To protect livestock/cattle use, chromium levels should be less than 0.05 mg/L and general irrigation water should not exceed 5 ppm in coarse soils or 20 ppm in firm soils [671].

Information from Moore [445]:

Reader caution: There may be some electronic transmission errors in the following (indented) text from Moore, so refer to the original hardcopy text for confirmation for use in critical applications and for documentation of the references in parentheses). This information provided with permission of senior author Stephen Moore for the sole purpose of preliminary information searching convenience [445]:

Frog tadpoles (*Rana hexadactyla*), which averaged 20 mm in length and 500 mg in weight, were subjected to a static bioassay to determine the 24-, 48-, 72-, and 96-hour LC50's for waterborne hexavalent chromium (as potassium chromate [K<sub>2</sub>CrO<sub>4</sub>] and potassium dichromate) (Khangarot et al., 1985).

Water chemistry in these studies included hardness of 20 ppm (as calcium carbonate) and pH of 6.2-6.7. The 24-, 48-, 72-, and 96-hour LC50 values for potassium chromate were 200, 200, 150, and 100 ppm, and for potassium dichromate were 75, 51.01, 46.82, and 42.59 ppm, respectively.

Teratogenic and other effects of chromium+6 to frog tadpoles (*Rana tigrina*) were studied by Abbasi and Soni (1984a). Tadpoles were exposed to waterborne concentrations of 0, 2, 5, or 7 ppm hexavalent chromium (as potassium dichromate). Water chemistry in these studies included hardness of 4.0 ppm total hardness and 3.0 ppm calcium hardness and pH of 6.1. Swimming behavior was altered in exposed tadpoles and affected tadpoles displayed erratic, fast, and twisting movements, and decreased tendency to surface for air. Tadpoles exposed to all concentrations of chromium+6 died within 72 hours; control tadpoles did not suffer mortality. Additionally, numerous deformities, including broadening of the eyes, reduction and curving of the tail fin, and protrusion of the alimentary canal, and other effects such as clustration of pigments on the dorsal side of the head, loss of pig...(sic)..5, or 7 ppm chromium+6.

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

NOTE: Drinking water is sometimes regulated as either Chromium III or Chromium VI, rather than total chromium. For details, see the entries for Chromium III and Chromium VI.

EPA 1996 IRIS information on Total Chromium [893]:

Maximum Contaminant Level Goal: 0.1 mg/L total chromium [893,952].

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 [893,952].  
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].

No tap water PRG given [868].

State Drinking Water Standards [940].

1. (AL) ALABAMA 50 ug/l [USEPA/Office of  
Water; Federal-State Toxicology and Risk  
Analysis Committee (FSTRAC). Summary of State  
and Federal Drinking Water Standards and  
Guidelines (11/93) [940].

2. (AZ) ARIZONA 50 ug/l [USEPA/Office of  
Water; Federal-State Toxicology and Risk  
Analysis Committee (FSTRAC). Summary of State  
and Federal Drinking Water Standards and  
Guidelines (11/93) [940].

State Drinking Water Guidelines [940].

1. (AZ) ARIZONA 120 ug/l [USEPA/Office of Water; Federal-State Toxicology and Risk Analysis Committee (FSTRAC). Summary of State and Federal Drinking Water Standards and Guidelines (11/93) [940].
2. (ME) MAINE 100 ug/l [USEPA/Office of Water; Federal-State Toxicology and Risk Analysis Committee (FSTRAC). Summary of State and Federal Drinking Water Standards and Guidelines (11/93) [940].
3. (MN) MINNESOTA 100 ug/l [USEPA/Office of Water; Federal-State Toxicology and Risk Analysis Committee (FSTRAC). Summary of State and Federal Drinking Water Standards and Guidelines (11/93) [940].
4. (MN) MINNESOTA 20000 ug/l [USEPA/Office of Water; Federal-State Toxicology and Risk Analysis Committee (FSTRAC). Summary of State and Federal Drinking Water Standards and Guidelines (11/93) [940].

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

The most significant anthropogenic point sources of chromium in surface waters and groundwaters are the waste waters from electroplating operations, leather tanning industries, and textile manufacturing [927]. In addition, deposition of airborne chromium is also a significant nonpoint source of chromium in surface water [927]..

A potential complication in comparing contaminants data is that different investigators have sometimes meant different things when they put the words "dissolved" or "total" in front of a reported measurement. In the case of nutrients, the "dissolved" portion is usually simply that portion which has passed through a 0.45-micrometer membrane filter and the "total" measurements implies that it was not filtered and includes both dissolved and other forms of the nutrient [141]. However, usage of the words dissolved and total has not been uniform in the past and there is still considerable debate about which methods should truly be considered "dissolved" or "total" (Merle Schlockey, USGS, personal communication).

Water bodies are often marked by heterogeneity of the distribution of undissolved materials [691]. The size of any effects depends on the difference in density of the

undissolved materials and the water, the size of the particles or bubbles of the materials, and various hydrodynamic factors such as the degree of turbulence in the water. Thus, undissolved inorganic materials in rivers and other natural water-bodies tend to increase in concentration with increasing depth because the particles tend to settle [691]. On the other hand, certain biological detritus may tend to rise towards the surface of the water because its density is less than that of water; oils also commonly demonstrate this effect markedly [691]. The surface microlayer is usually higher in concentration of many metallic and organic contaminants than the water column further down.

If the only change one makes is to use the prefix "dissolved" rather than the prefix "total" in an otherwise identical water quality standard, the effect can be a weakening of the standard related to total loading of a system. Many contaminants which are not currently dissolved can become dissolved at a later time, when encountering different conditions (perhaps downstream), such as changes in pH, additions of surfactants or humic substances, bioturbation, methylating organisms, and various other physical, chemical, or biological changes.

One problem with relying too heavily on dissolved fractions of metals is that the dissolved fraction misses the metals carried by colloids. Colloids were found to carry toxic metals 140 miles downstream of mining sources in Leadville, Colorado, to be repeatedly washed from flood deposited lowlands back into the river year after year in spring runoff (Briant Kimball, USGS Salt Lake City, as quoted in U.S. Water News, April 5th, 1995).

See Laboratory section below for EPA generic (guesstimate) conversion factors to convert total to dissolved concentrations.

Some environmental toxicologists make the argument that dissolved metals in surface water and porewaters represent most of what is bioavailable and thus "total" metals parameters are not good as a measure of potential biological effects. This is mostly true in many situations, but it should be kept in mind that fish and other aquatic organisms do not typically live in filtered water and that many fish and other aquatic organisms live in the sediments and in other situations in which they come in contact with toxic or otherwise harmful compounds (as certain colloids, precipitates, oxides, adsorbed metals), etc. Sometimes the effect of total metals is partially related to physical or chemical aspects, such as when ferric oxide coats or covers benthic organisms. Another factor to consider: contaminants carried

downstream by erosion of bottom sediments or colloids can be mobilized when they come in contact with different physical/chemical environments downstream (for example, a tributary bringing low pH into the system).

Misc. Notes on colloids (Briant Kimball, USGS, Salt Lake City Office, Personal Communication, 1995):

There is no question that dissolved metals are critical to fish and invertebrates, but less well recognized is the potential impact and movement of metals in colloids. The possibility of having colloidal material present means there is a readily available supply of metals in a state in which the metals can quickly be reduced and mobilized. In river banks, reducing environments form just under the surface quickly. Toxic metals of concern would include zinc, lead, copper, and cadmium.

Colloids do move in surface water (for example, transport of metal in colloids 140 miles downstream of Leadville, CO), but also in groundwater, especially related to radionuclides.

Colloidal metals may effect biota more than is widely recognized. Brown trout are effected by colloids which travel kind of like dissolved fractions, don't settle out. There may be little understood colloidal pathways of metals to fish, for example. Colloidal metals become part of the caddis cast which are ingested, once part of acid gut, metals can be released. On the Arkansas River of Colorado below Leadville, the dissolved metals have gone down with treatment, but Will Clements of CSU has discovered the toxicity has not been reduced to the same extent as have the dissolved metals. Treatment has not eliminated colloidal fractions loaded with cadmium and copper, and this is possibly impacting the fish.

In rivers, there is annual flushing of the colloids, loads are much greater during runoff.

**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):

Texas: The statewide 90th percentile value for chromium was 72.1 mg/kg dry weight [7].

Great Lakes Harbors, EPA 1977: Sediments having concentrations higher than 75 mg/kg dry weight were classified as "heavily polluted" (27-75 considered moderately polluted) [145].

Illinois EPA, 1984: Sediments having concentrations higher than 23.0 mg/kg dry weight were classified as "elevated" [145].

Highway Runoff, 1989: Detention pond sediments receiving runoff from highways averaged 20 mg/kg dry weight of chromium; the cypress wetlands the detention pond effluent was routed to, by contrast, had a median value of 2 mg/kg chromium, indicating most was removed by the detention pond [220].

In a previous study by the Texas Water Quality Board, the chromium level in sediments from Beltline Road (6.5 miles downstream of our site 11) was 140 mg/kg, the highest recorded in the State at that time [74]. The highest levels of chromium (53.0 to 140.0 mg/kg) were found in sediment samples from sites 8 through 12 (using our site numbers), with much lower concentrations upstream [74]. Chromium concentrations in water from the area were also elevated [71]. Sediment concentrations of chromium from our sites 9 through 12 exceeded the statewide 90th percentile level, 72.1 mg/kg, in at least 50% of the historical records from 1974 to 1985 [7].

The most severely affected sites in Ontario include St. Marys River system with concentrations of 31,000 ug/g dry weight in Tannery Bay, and the Welland River downstream from a steel manufacturing plant, where the concentrations of chromium exceeded 5120 ug/g dry weight compared to 10 ug/g dry weight at the upstream control site [926].

Concentrations ranged from up to 1920 ug/g dry weight (dw) in Detroit River sediments to 564 ug/g dw in Hamilton Harbor sediments [926].

NOAA National Status and Trends Program (1984-1990) [698]: High concentration for chromium in fine-grained sediment (n=233) = 230 ug/g dry weight at 4.6% TOC dry weight. Chromium levels are particularly high as a result of naturally high levels in the Pacific Northwest,

where a large proportion of the total sampling took place [698]. The above concentration was adjusted for sediment grain-size in the following way: the raw concentrations were divided by the fraction of particles less than or equal to 64 um. "High" NOAA concentrations are equal to the geometric mean plus one standard deviation on the log normal distribution [696].

NOTE: Fine-grained sediment would typically contain more chromium than coarse-grained sediment, and sediments higher in total organic carbon (TOC) would typically have more chromium than sediments which are similar except for being lower in TOC, which is why NOAA and many others are now normalizing sediment values for grain size, and reporting TOC.

Analyses of sewage sludges from 50 publicly owned treatment works by the U.S. Environmental Protection Agency (1985): The mean concentration of chromium was 427.9 ppm (dry weight) [347].

Analyses of 74 Missouri sludges (1985): Chromium (median) 85.5 ppm (dry weight), chromium (range) 10-12,000 ppm (dry weight) [347].

**Sed. Typical** (Sediment Concentrations Considered Typical):

NOAA National Status and Trends Program (1984-1990) [698]: Geometric mean for chromium in fine-grained sediment (n=233) = 110 ug/g dry weight at 1.4% TOC dry weight. Chromium levels are particularly high as a result of naturally high levels in the Pacific Northwest, where a large proportion of the total sampling took place [698]. The above concentration was adjusted for sediment grain-size in the following way: the raw concentrations were divided by the fraction of particles less than or equal to 64 um.

NOTE: Fine-grained sediment would typically contain more chromium than coarse-grained sediment, and sediments higher in total organic carbon (TOC) would typically have more chromium than sediments which are similar except for being lower in TOC, which is why NOAA and many others are now normalizing sediment values for grain size, and reporting TOC.

Great Lakes Harbors, EPA 1977: Sediments having sediment concentrations lower than 25.0 mg/kg dry weight were classified as "non-polluted" [145].

International Joint Commission, 1988: The International

Joint Commission considered <37.1 mg/kg dry weight as a background sediment level [145]. The control site in one Great Lakes study had a sediment concentration of 23.5 mg/kg dry weight [145].

**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):

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Sediment Concentrations. To be considered unlikely to represent an ecological risk, field concentrations should be below all of the following benchmarks in mg/kg (ppm) dry weight [652]:

For CAS 7440-47-3 (CHROMIUM):

LOWEST EFFECT LEVEL (ONTARIO MOE): 26 mg/kg

EFFECTS RANGE - MEDIAN (NOAA): 370 mg/kg

EFFECTS RANGE - LOW (NOAA): 81 mg/kg

Various Other Concern Levels for Chromium Sediment Concentrations (Dry Weight):

EPA Region 6, 1973: The concentration proposed by EPA Region 6 as a guideline for determining acceptability of dredged sediment disposal was 100 mg/kg [143].

Ontario Ministry of the Environment guidelines for open lake disposal of sediments (1986): The guideline for chromium is 25 ppm [347].

Previous benchmark was the same: Ontario, 1978: The concentration proposed by the Ontario Ministry of the Environment as a threshold for evaluations of dredging projects was 25.0 mg/kg [145].

Wisconsin interim criteria for sediments from Great Lakes harbors for disposal in water (1985): Chromium should not exceed 100 ppm (dry weight) [347].

International Joint Commission, 1988: The IJC suggested sediment concentrations not exceed background levels of 37.1 mg/kg [145].

AET 1988: The apparent effects threshold concentrations for chromium in sediments proposed for Puget Sound ranged from 260 mg/kg dry weight (Benthic Species) to 270 mg/kg dry weight (amphipods) [416]. Although the authors of the Puget Sound AETs have cautioned that Puget Sound AETs may not be appropriate for comparison with data from other geographic areas, so few concern levels for this chemical have been published that the proposed Puget Sound concern level is included in this text as an item of interest.

NOAA 1995 Concern Levels for Coastal and Estuarine Environments: After studying its own data from the National Status and Trends Program as well as many literature references concerning different approaches to determining sediment criteria, NOAA suggested that the potential for biological effects of this contaminant sorbed to sediments was highest in sediments where its concentration exceeded the 370 ppm dry weight Effects Range-Median (ERM) concentration and was lowest in sediments where its concentration was less than the 81 ppm dry weight Effects Range-Low (ERL) concentration [664]. To improve the original 1990 guidelines [233], the 1995 report included percent (ratios) incidence of effects for ranges below, above, and between the ERL and ERM values. These numbers represent the number of data entries within each concentration range in which biological effects were observed divided by the total number of entries within each range [664]:

<ERL	2.9
ERL-ERM	21.1
>ERM	95.0

Ontario Ministry of the Environment Freshwater Sediment Guidelines, 1993: Lowest effect level: 26 mg/kg dry weight. Severe effect level: 110 mg/kg dry weight [761].

St. Lawrence River Interim Freshwater Sediment Criteria, 1992: No effect: 55 mg/kg dry weight. Minimal effect: 55 mg/kg dry weight. Toxic effect: 100 mg/kg dry weight [761].

Environment Canada Interim Sediment Quality  
Assessment Values, 1994: Threshold effect level:  
37.3 mg/kg dry weight. Probable Effect Level:  
90.0 mg/kg dry weight [761].

**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):

Most of the chromium released into water will ultimately  
be deposited in the sediment [927]. See also: Fate  
sections.

**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):

Elevated concentrations (over 100 ug/g (ppm) dry weight  
compared to 38 ug/g (ppm) dry weight in uncontaminated  
soils nearby) were reported in soils adjacent to two  
scrap yards in Winnipeg, Canada [926]. Levels of  
chromium in soils around the smelter at Belledune, New  
Brunswick, were 40 to 120 ug/g (ppm) dry weight [926].

The average chromium concentrations in surface soils near  
two wood treatment facilities in Atlantic Canada were  
1170 and 1760 ug/g dry weight [926].

Analyses of sewage sludges from 50 publicly owned treatment works by the U.S. Environmental Protection Agency (1985): The mean concentration of chromium was 427.9 ppm (dry weight) [347].

Analyses of 74 Missouri sludges (1985): Chromium (median) 85.5 ppm (dry weight), chromium (range) 10-12,000 ppm (dry weight) [347].

**Soil. Typical** (Soil Concentrations Considered Typical):

EPA 1981: 100 mg/kg dry weight not considered elevated [83].

USGS 1984: Total chromium concentrations in conterminous U.S. soils range from 1.0 to 2,000 mg/kg, with a mean of 37.0 mg/kg [927].

Igneous Rocks (Earth's Crust) Concentrations: EPA 1981: 100 mg/kg dry weight [83].

The mean soil concentration of chromium in the U.S. was 53 ppm (range 1 to 1,500 ppm) [347].

The concentration of chromium in soils from 173 sites in Canada ranged from 10 to 100 ug/g (ppm) dry weight (mean value 43 ug/g (ppm) dry weight) [926].

In soil, chromium concentrations commonly range from 5 to 300 ppm, depending on the parent material [445]. Soils derived from serpentine strata may contain 500 to 62,000 ppm chromium [445].

The abundance of chromium in various materials is as follows: 80-200 ppm in the continental crust, 125 ppm avg; 1,000-3,400 ppm in ultramafic igneous rocks, 1,800 ppm avg; 40-600 ppm in basaltic igneous rocks, 220 ppm avg; 2-90 ppm in granitic igneous rocks, 20 ppm avg; 30-590 ppm in shales and clays, 120 ppm avg; and 10-1,000 ppm in coals, 20 ppm avg. (Bowen HJM ed; Trace Elements in Biochem, 1966, as cited in NAS; Medical and Biological Effects of Environmental Pollutants: Chromium p.9, 1974) [366].

**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):

Other Maximum Allowable Concentration (MAC) levels for chromium: 100 ppm dry weight (Stuttgart, Germany), 600 (London) [719]

Proposal of European Economic Commission for MAC in soils treated with sewage sludge: 50 ppm dry weight (London) [719].

Proposal of Ontario Ministry of Agriculture and Food for MAC in soils treated with sewage sludge: 120 ppm dry weight (published in Tokyo; work done for Ontario) [719].

Soviet Union Maximum Allowable Concentration in Soils, 1984: 0.05 mg/kg [347].

The 1987 soil (clean up) criteria given by the New Jersey Department of Environmental Protection for chromium is 100 mg/kg dry weight [347,386].

In 1981 the U.S. Environmental Protection Agency proposed 1000 ppm as an upper limit for chromium for sewage sludges suitable for land application [391].

Soil criteria for evaluating the severity of chromium contamination under the Dutch Soil Cleanup (Interim) Act (1982): Background concentration or detection limit of chromium in soil is 100 ppm, moderate soil concentration is 250 ppm, and threshold value of chromium in soil is 800 ppm [347].

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].

Soil cleanup criteria for decommissioning industrial sites in Ontario for Chromium (total) (1987): For agricultural land chromium should not exceed 120 ppm, for residential and parklands chromium should not exceed 1,000 ppm, and for commercial and industrial lands chromium should not exceed 1,000 ppm [347].

Suggested cleanup guidelines for inorganic contaminants in acidic soils in Alberta for chromium (1987): Acceptable level of chromium for acidic soils (pH <6.5) is 600 ppm [347].

Maximum cumulative addition of metals (kg/ha) from sewage sludge recommended for privately owned

Missouri farmland (1988): For a soil with a cation exchange capacity (CEC) of less than 5 meq/100g chromium should not exceed 560 ppm. For a soil with a CEC between 5 and 15 chromium should not exceed 1,120 ppm. For a soil with a CEC greater than 5 chromium should not exceed 2,250 ppm [347].

Cumulative amounts of metals per hectare that may be added to New York State soils with sewage sludge (1988): For productive agricultural soils chromium addition should not exceed 336 ppm, for less productive soils chromium should not exceed 500 ppm [347].

Maximum cumulative additions (kg/ha) of metals from sewage sludge that may be added to Vermont soils, by soil texture (1984): For loamy sand chromium should not exceed more than 140 ppm. For fine sandy loam chromium should not exceed 280 ppm. For clay loam chromium should not exceed 560 ppm [347].

#### **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 dw of Cr+6 induced iron chlorosis in oats, retarded stem development in tobacco, and inhibited the uptake of micronutrients by soybeans [926].

Levels of chromium (ppm dry weight) considered phytotoxic: 100 (Vienna), 100 (Warsaw), 100 (Warsaw), 75 (Ontario) [719].

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Terrestrial Plants. To be considered unlikely to represent an ecological risk to terrestrial plants, field concentrations in soil should be below the following dry weight benchmark for soil [651]:

For CAS 007440-47-3 (CHROMIUM), the benchmark is 1 mg/kg dry weight in soil.

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].

**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) for total chromium, 1995 [868]:

Residential Soil: 210 mg/kg wet wt.

Industrial Soil: 450 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:

None given for total chromium (see chromium III and VI entries) [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):

Chromium toxicity to plants is moderate [951].

Chromium (III) in soil is mostly present as insoluble carbonate and oxide of chromium(III); therefore, it will not be mobile in soil [927]. The solubility of chromium(III) in soil and its mobility may increase due to the formation of soluble complexes with organic matters in soil [927]. A lower soil pH may facilitate complexation [927]. Chromium has a low mobility for translocation from roots to the above ground parts of plants [927].

**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:

The following ranges of concentrations of chromium in plants (dry weight) were found in samples collected along metals-impacted Soda Butte Creek in Yellowstone Park in 1992 (Daniel Norton, USGS, personal communication, 1995):

Grasses: 0.25 to 4.13 ppm  
Lichen: 37.92 ppm (one sample)  
Moss: 31-300 ppm  
Willow: 0.7 to 1.98 ppm

Most chromium in soil is not available for plant uptake because of adsorption, complexation with minerals, or precipitation; chromium usually occurs in plant tissues in concentrations of a few ppm, although much higher concentrations have been found in plants growing on infertile, serpentine soils [445].

The majority of chromium in plants is taken up from the soil, although most soil chromium is biologically unavailable. Uptake may be affected by chromium form, pH, chelation with other soil

compounds, and plant species. Chromium is not actively transported throughout the plant; ninety-eight percent of labelled trivalent or hexavalent chromium has been found to be retained in the roots [445].

**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:

Midge larvae and mayflies (Hexagena) collected in 1985 from Midland Bay and Penetang Bay (Lake Huron) had 1.2 and 1.7 ug/g wet weight of Cr, compared to 1.3 ug/g at the control area [926].

Kranzberg (1985) reported higher concentrations of chromium in benthos larvae (5.7 ug/g dry weight) in lakes of the Muskoka-Haliburton area, Ontario, compared to the values for adult benthic species (1.0 ug/g dry weight) from the same water [926].

Chromium does not accumulate to the same extent in both oysters and mussels. Therefore, the following information summarizes data gathered on both oysters and mussels from the NOAA National Status and Trends (NS&T) Program for the year 1990 [697]:

For chromium in oysters (n=107), the Geometric Mean was 0.48 ug/g dry and the "high" concentration was 0.93 ug/g dry weight [697]. For chromium in mussels (n=107), the Geometric Mean was 1.7 ug/g dry and the "high" concentration was 3.0 ug/g dry weight [697]. NOAA "high" concentrations are equal to the geometric mean plus one standard deviation on the log normal distribution [696].

Concentrations in Texas, Rio Grande at Big Bend National Park: (The following text is quoted from the Big Bend Report [65] for reference comparison with values from other areas): Chromium

concentrations above the detection limit (0.10 mg/kg) were found in 16 of 18 tissue and sediment samples analyzed for metals. Maximum Levels: The two highest concentration of chromium in Big Bend Rio Grande River samples was a composite sample of aquatic insects (2.4 mg/kg).

Other Trinity River samples above 2.0 mg/kg chromium included a crayfish sample and a composite sample of asiatic clam tissue [201]. Chromium has a higher bioaccumulative potential in clams and crayfish than in fish [83].

#### **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:

The highest concentrations of chromium in 6 studies of edible fish tissues in several states was 13.93 mg/kg wwt [57]. The highest level in all but one of these 6 studies was 1.42 mg/kg wwt [57]. Fish do not accumulate much chromium in their bodies from water [927].

A survey of Pennsylvania fish from 16 sites revealed detectable chromium at 4 sites, with whole-body concentrations of chromium ranging from 0.1 to 0.26 mg/kg [57]. Based on our review of data from several U.S. Fish and Wildlife Service studies in the southwest, we consider chromium levels above 0.8 mg/kg in fish and wildlife tissues to be elevated [78,79,201]. That level was exceeded by 4 of 14 Rio Grande tissue samples [65].

Elwood et al., (1980) reported that average chromium concentrations in freshwater fish are generally less than 1 ppm (wet weight) [445].

Gradient Monitoring Levels: Twelve of 32 fish from the heavily agricultural areas of the lower Rio Grande Valley far downstream of Big Bend National

Park had chromium values exceeding 0.20 mg/kg and 6 of 32 had values exceeding 0.8 mg/kg (Larry Gamble, U.S. Fish and Wildlife Service, personal communication). However, different fish species and at least one brackish\marine fish species were analyzed for chromium in the lower Rio Grande study, while all fish collected at Big Bend National Park were freshwater species. Therefore, the fish data for chromium from these two Rio Grande sites are not directly comparable [202].

The chromium levels (0.14 to 0.54 mg/kg) in 3 composite samples of mosquitofish from the Rio Grande were significantly lower than those found in mosquitofish from the upper Trinity River [201].

Upper Trinity River: (The following text is quoted from the Trinity River Report [201] for reference comparison with values from other areas): Chromium concentrations above the detection limit (0.20 mg/kg) were found in 69 of 77 Trinity River samples. Among the two highest concentrations of chromium was a composite whole-body sample of mosquitofish (9.7 mg/kg) from a Fort Worth storm drain site receiving runoff from a large metal scrap yard [201].

Gradient Monitoring Levels [201]: Chromium showed a tendency to increase from upstream to downstream in Trinity River mosquitofish.

Mosquitofish from urban areas of the upper Trinity River had concentrations of chromium ranging from 0.2 to 1.7 mg/kg. Mosquitofish from rural sites on the Rio Grande River at Big Bend National Park had significantly lower concentrations of chromium than mosquitofish from the urbanized upper Trinity River [65]. Chromium concentrations in Big Bend National Park mosquitofish ranged from 0.14 to 0.54 mg/kg [65].

**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].

Predator Protection Level Related to Oral Dose:

Little is known about the effects of elevated tissue levels of chromium on fish and wildlife. Apparently, the only chromium level that has been proposed as a protective standard for animal tissues is 0.20 mg/kg [24].

Information from Moore [445]:

Reader caution: There may be some electronic transmission errors in the following (indented) text from Moore, so refer to the original hardcopy text for confirmation for use in critical applications and for documentation of the references in parentheses). This information provided with permission of senior author Stephen Moore for the sole purpose of preliminary information searching convenience [445]:

In domestic avian species, hexavalent chromium (as sodium chromate) at concentrations of 30 and 100 ppm in the diet had no effect on performance (weight gain and feed:gain ratio) of growing chicks over a 3-week period (Romoser et al., 1961).

Few data are available on the toxicity of long-term exposure to chromium in wild birds. Heinz and Haseltine (1981) studied the effects of dietary chromium+3 exposure in black ducks (*Anas rubripes*). Hens were fed duck breeder mash diets (<10% moisture) nominally containing 0, 20, or 200 ppm chromium potassium sulfate for approximately 5 months prior to egg laying. Ducklings from these hens were then fed duck starter mash containing the same dietary chromium+3 concentrations as the hens. When one-week-old, the ducklings were exposed to a fright stimulus to test avoidance behavior. No significant difference in response between the treatment groups and the control was measured.

Haseltine (pers. comm., May 8, 1990, S.D. Haseltine, Director, USFWS-NPWR, Jamestown,

ND) conducted an experiment to test the effects of dietary chromium on growth, survival, reproduction, and residue accumulation in American black ducks. Adult ducks and ducklings were fed dry, commercial duck mash diets (<10% moisture) nominally containing 0, 10, or 50 ppm trivalent chromium (as chromium potassium sulfate). Although weights of adult birds were unaffected by chromium+3 ingestion during the study (~7 months in duration), those ducks exposed to chromium+3 concentrations of 50 ppm had greater mortality than ducks exposed to 10 ppm chromium+3 and those on control diets. Egg laying, fertility, and embryonic mortality in ducks were not different among treatments; however, hens in the high-chromium+3 group raised a smaller proportion of their broods to 10 weeks of age than did hens in the lower chromium+3 or control groups. Growth of ducklings was initially depressed and survival of offspring (after 10 weeks) was reduced in both chromium+3 diet groups. With the exception of hen tibias, chromium+3 residues in tissues of adults and young ducks were not related to concentration of chromium+3 ingestion.

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

Tissue levels in excess of 4.0 mg total chromium/kg dry weight should be viewed as presumptive evidence of Cr contamination, although the significance of tissue Cr residues is unclear [24].

Turtle Concentrations in Texas: Rio Grande at Big Bend National Park: (The following text is quoted from the Big Bend Report [65] for reference comparison with values from other areas): Among the maximum Levels: a composite sample of softshell turtles (0.96 mg/kg chromium). Directly comparable data for the Rio Grande and Trinity Rivers is available for softshell turtles. The chromium level in one composite sample of softshell turtles from Castolon was 0.96 mg/kg. For contrast, the geometric mean of chromium concentrations in 22 softshell turtle samples from the lower Rio Grande Valley was 0.34 mg/kg [202], and chromium concentrations in softshell turtles from four Trinity River sites ranged from 0.10 to 0.30 mg/kg [201]. Maximum Levels: The two highest concentrations of chromium were a fatty tissue

sample (6.0 mg/kg) from a composite of three Mississippi map turtles [201].

Studies in ducks collected in northern New Jersey provided estimates of chromium concentrations in duck liver tissue. Chromium concentrations in male black ducks, scaup, and mallards were 2,053, 1,539, and 1,735 ppb (wet weight), respectively [445].

**Tis.Human:**

A) Typical Concentrations in Human Food Survey Items:

The typical chromium levels in most fresh foods are less than 50 ug/kg (Fishbein 1984) [927]. Chromium (III) occurs naturally in many fresh vegetables, fruits, meat, yeast, and grain [927]. Various methods of processing, storage, and preparation can alter the chromium content of food [927]. Acidic foods in contact with stainless steel cans or cooking utensils might contain higher levels of chromium because of leaching from stainless steel [927].

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):

Legal Limits for Concentrations in Fish and Fishery Products:

The only legal limit found so far was 1.0 mg/kg (Hong Kong) [216,418]. The U.S. apparently has no limit [216,418].

RfD: Like Chromium VI (CAS 18540-29-9), Chromium in general (CAS 7440-47-3) has an RfD of 5.0E-03 mg/kg/day and is classified as a class A carcinogen [952].

Slope Factor: 4.2E+02 mg/kg/day [868].

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

Chromium can be measured in the hair, urine, serum, red blood cells, and whole blood [927]. However, since chromium(III) is an essential nutrient, low levels of chromium are normally found in body tissues and urine [927].

**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:

The bioconcentration factor (BCF) for chromium (VI) in rainbow trout (*Salmo gairdneri*) is ~1 [927]. In bottom-feeder bivalves, such as the oyster (*Crassostrea virginica*), blue mussel (*Mytilus edulis*), and soft shell clam (*Mya arenaria*), the BCF values for chromium (III) and chromium (VI) may range from 86 to 192 [927]. The bioavailability of chromium (III) to freshwater invertebrates (*Daphnia pulex*) decreased with the addition of humic acid [927]. 1989) [927]. This decrease in bioavailability was attributed to lower availability of the free form of the metal due to its complexation with humic acid [927]. Based on this information, chromium is not expected to biomagnify in the aquatic food chain [927]. Although higher concentrations of chromium have been reported in plants growing in high chromium-containing soils (e.g., soil near ore deposits or chromium-emitting industries and soil fertilized by sewage sludge) 6 [927].

Preliminary data suggests the potential for bioaccumulation or bioconcentration of chromium is moderate for the following biota: mammals, birds, and fish [83]. Chromium rapidly accumulates in the testes and then in the epididymes after injection of a tracer dose, thus suggests a possible incorporation of chromium into sperm [366]. In rats, chromium salts show highest uptake in ovaries, spleen, kidneys, and liver; and chromium as glucose tolerance factor shows highest uptake in the liver, uterus, kidneys, and bone [366].

High accumulations of Cr have been recorded among organisms from the lower trophic levels, but there is little evidence of biomagnification through food chains [24]. The potential for accumulation is considered high to very high for mosses, lichens, algae, mollusks, crustacea, lower animals, and higher plants [83]. The best potential mediums for biological monitoring appear to include animal hair, mammal spleens, mosses, lichens, clams, algae, and higher plants [83]. In general, plants seem to show the best gradients, but some animals do as well [83]. Irwin found mosquitofish to be acceptable for gradient monitoring of chromium [201].

Biological Half-Life [366]:

The elimination curve for chromium as measured by whole-body counting has an exponential form. In rats, 3 different components of the curve have been identified with the half-times of 0.5, 5.9, and 83.4 days, respectively. [Friberg, L., Nordberg, G.F., Kessler, E. and Vouk, V.B. (eds). Handbook of the Toxicology of Metals. 2nd ed. Vols I, II.: Amsterdam: Elsevier Science Publishers B.V., 1986.,p. V2 193].

#### Bioaccumulation [445]:

Chromium is accumulated across a concentration gradient in some organisms, particularly aquatic and marine biota; however, biomagnification in food chains does not appear to occur. Chromium has been shown to be concentrated by tubificid worms after ingestion of chromium-enriched bacteria. When tropical fish (*Hyphessobrycon serpae*) consumed the worms, tissue chromium concentrations were increased after 4 days. Callahan et al. (1979) tabulated reported concentration factors for chromium (defined as the "ratio of the concentration of the element in the organism in ppm (wet weight) divided by the concentration of the element in water (ppm)") for various aquatic plants and animals. Examples of these factors include: 200 for freshwater fish, 2,000 for freshwater invertebrates, 4,000 for freshwater plants, 100 for crustacean muscle, and 70 for fish muscle.

#### Bioconcentration [940]:

Snails showed an accumulation factor of  $1 \times 10^6$ . /Total chromium/ [Levine EP; Science 133: 1352-3 (1961) as cited in Nat'l Research Council Canada; Effects of Chromium in the Canadian Envir p.50 (1976) NRCC No.15017].

*Leptospermum scoparium*, a shrub, showed an accumulation factor of  $1 \times 10^3$  compared to normal plants. /Total chromium/ [Lyon GL et al; Planta 88: 282-7 (1969) as cited in Nat'l Research Council Canada; Effects of Chromium in the Canadian Envir p.50 (1976) NRCC No.15017].

Seaweed showed an accumulation factor of  $1 \times 10^2$ . /Total chromium/ [Boothe PN, Knauer GA; Limnol Oceanogr 17: 270-4 (1974) as cited in Nat'l Research Council Canada; Effects of Chromium in the Canadian Envir p.50 (1976) NRCC No.15017].

#### **Interactions:**

The presence of > 100 ppm Chromium may adversely affect the biodegradation of sewage sludge. /Total chromium/ (Nat'l Research Council Canada; Effects of Chromium in the Canadian Envir p.91, 1976, NRCC No.15017) [366].

In plants, chromium (Cr) 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 (Turner MA, Rush RH; Soil Soc Am Proc 35: 755, 1971, as cited in Nat'l Research Council Canada; Effects of Chromium in the Canadian Envir p.88, 176, NRCC No.15017) [366,940].

The 96-hour LC50 of waterborne trivalent chromium to rainbow trout fry was determined to be 11.2 ppm by Bills et al. (1977) [445]. Previous exposure to low and high concentrations of the

polychlorinated biphenyl, Aroclor 1254, decreased the LC50 values of chromium+3 to 9.0 and 7.05 ppm, respectively [445].

HSDB [940]: Rats given 1 intratracheal intubation of 10 mg powder chromium alone or ... With ... Methylcholanthrene & killed @ ... Intervals up to 12 wk. Squamous-cell carcinomas of lung developed ... In 7/12 rats given 5 mg methylcholanthrene+chromium 3/12 given 1 mg methylcholanthrene+chromium ... 3/7 Given 5 mg methylcholanthrene ... 1/8 Given 1 mg methylcholanthrene & in 0/12 given chromium alone. /No controls reported/ [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-1985. (Multivolume work).,p. V23 256 (1980)].

#### 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].

Plants take up chromium from soil, groundwater, surface water, sewage sludge, fertilizers and air pollution [83]. Animals take up chromium from industrial sources, contaminated water, and contaminated food [83]. Known sources of chromium include metal platers and a wide variety of chemical, photography, metal plating, scrap metal, machine shop, power plant, and industrial facilities [24,57]. Elevated chromium levels have been found in some samples of sewage sludge from the Dallas/Fort Worth area (Ron Carlson, City of Fort Worth, personal communication). Chromium is also present in the leachate of some municipal landfills [80].

A variety of household products, such as cleaning agents, contain chromium. It is also released from wood products treated with preservatives containing chromium. The mainstream smoke of Canadian cigarettes has been estimated to contain 0.147 ug per cigarette [926].

#### Major Uses [940]:

Increases resistance & durability of metals; chromeplating other metals [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 317].

Nuclear & high temperature research [Sax, N.I. and R.J. Lewis, Sr., eds., Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 280].

Pigments for floor covering products, paper, cement, and asphalt roofing. /Total chromium/ [USEPA; Background

Document, Resource Conservation and Recovery Act Subtitle C: Identification and Listing of Hazardous Waste p.189 (1980)].

Used in coloring glass an emerald color. [Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. B-13].

Component of stainless & heat resisting steels component of stainless & heat resisting steels [SRI].

Component of full alloy steel [SRI].

Component of high strength, low alloy, & electric steels [SRI].

Component of superalloys, cast irons, & carbon steel [SRI].

Component of other alloys-eg, nonferrous & magnetic [SRI].

Component of tool steel & welding materials [SRI].

1) Use in fabrication of alloys; 2) use in preparation of alloy steels to enhance corrosion and heat resistance; 3) use in fabrication of plated products for decoration or increased wear resistance; 4) use in production of non-ferrous alloys to impart special qualities to the alloys; 5) use in production and processing of insoluble salts; 6) use as chemical intermediates; use in textile industry in dyeing, silk treating, printing, and moth proofing wool; 7) use in leather industry in tanning; use in photographic fixing baths; 8) use as catalysts for halogenation, alkylation, and catalytic cracking of hydrocarbons; and 9) use as fuel additives and propellant additives; in ceramics. /Chromium metal and insoluble chromium salts/ [Mackison, F. W., R. S. Stricoff, and L. J. Partridge, Jr., eds., NIOSH/OSHA - Occupational Health Guidelines for Chemical Hazards. DHHS(NIOSH) PublicationNo. 81-123 (3 VOLS). Washington, DC: U.S. Government Printing Office, Jan. 1981. 3].

Chromium and its compounds are used in metal alloys such as stainless steel; protective coatings on metal; magnetic tapes; and pigments for paints, cement, paper, rubber, composition floor covering and other materials. Other uses include organic chemical synthesis, photochemical processing and industrial water treatment. In medicine, chromium compounds are used in astringents and antiseptics. /Chromium and its compounds/ [DHHS/NTP; Fourth Annual Report On Carcinogens p.58 (1985) NTP 85-002].

Chromium encounters many industrial applications, including its uses in steel and nonferrous alloys, metal-plating, refractory materials, chromate pigments and chromate preservatives. /Chromium/ [Baselt RC; Biological Monitoring Methods for Industrial Chemicals p.81 (1980)].

Constituent of inorg pigments. /Total chromium/ [Sax, N.I. and R.J. Lewis, Sr., eds., Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 280].

Sensitizer in photographic industry; preparation of chromates. /Total chromium/ [Browning, E. Toxicity of Industrial Metals. 2nd ed. New York: Appleton-Century-Crofts, 1969. 120].

(51)Chromium is used as a radioisotopic tracer. /(51)Chromium isotope/ [NAS; Medical and Biological Effects of Environmental Pollutants: Chromium p.3 (1974)].

#### Natural Sources [366]:

Chromium is found in nature only in the combined state & not as the element. ... [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-1985. (Multivolume work).,p. V2 108 (1973)].

Chromium is widely distributed; avg concn 125 mg/kg in the continental crust, but rare in natural waters. /Chromium and chromium compd/ [USEPA; Ambient Water Quality Criteria Doc: Chromium p.C-4 (1980) EPA 440/5-80-035].

Present in small quantities in all soils & plants & ... Considered agriculturally as a deleterious element. Certain soils with a relatively high content (0.2-0.4%) Are said to be infertile; citrus trees grown on them show yellowing of foliage ... . [Browning, E. Toxicity of Industrial Metals. 2nd ed. New York: Appleton-Century-Crofts, 1969. 119].

Iron chromite (FeO.Cr<sub>2</sub>O<sub>3</sub>), which is found/ in nature only in the combined state & not as the element. ... Derived mainly from chromite (FeO.Cr<sub>2</sub>O<sub>3</sub>) ... found in considerable quantities in rhodesia, russia, south africa, new caledonia & the philippines & contains 40-50% chromium ... . [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-1985. (Multivolume work).,p. V2 108 (1973)].

Chromium occurs in nature mostly as chrome iron ore (FeO.Cr<sub>2</sub>O<sub>3</sub>). Chromium is present in small quantities in all soils & plants, @ 1-2.5 Ppb in sea water, & @ about 200 ppm in the earth's crust. The normal human adult body contains about 6 mg cr, with tissue concn of 0.02-0.04 Ppm Cr on dry wt basis. [Venugopal, B. and T.D. Luckey. Metal Toxicity in Mammals, 2. New York: Plenum Press, 1978. 248].

It is present in minor amt in igneous rocks & is much more abundant in basic & ultrabasic types than in the more silicic types of rocks. [National Research Council. Drinking Water & Health Volume 1. Washington, DC: National Academy Press, 1977. 241].

The most common meteorites, ie chondrites, contain 3,000 ug/g (ppm) chromium. /Total chromium/ [NAS; Medical and Biological Effects of Environmental Pollutants: Chromium p.2 (1974)].

Chromium in air associated with large particles (> 5 um diam) originates from wind blown soil and soil forming processes. /Total chromium/ [Nat'l Research Council Canada; Effects of Chromium in the Canadian Envir p.26 (1976) NRCC No.15017].

The abundance of chromium in various materials is as follows: 80-200 ppm in the continental crust, 125 ppm avg; 1,000-3,400 ppm in ultramafic igneous rocks, 1,800 ppm avg; 40-600 ppm in basaltic igneous rocks, 220 ppm avg; 2-90 ppm in granitic igneous rocks, 20 ppm avg; 30-590 ppm in shales and clays, 120 ppm avg; and 10-1,000 ppm in coals, 20 ppm avg. /Total chromium/ [Bowen HJM ed; Trace Elements in Biochem (1966) as cited in NAS; Medical and Biological Effects of Environmental Pollutants: Chromium p.9 (1974)].

#### Artificial Sources [366]:

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. /Total chromium/ [Nat'l Research Council Canada; Effects of Chromium in the Canadian Environment p.36 (1976) NRCC No 15017].

It could occur as water pollutant from chrome chemical plants or in losses during pigment prodn or leather tanning operations. /TOTAL CHROMIUM/ [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to

Man. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-1985. (Multivolume work).,p. V2 106 (1980)].

The two largest sources of chromium emission in the atmosphere are from the chemical manufacturing industry and combustion of natural gas, oil, and coal. Other sources include wind transport from road dust, cement producing plants because cement contains chromium, the wearing down of asbestos brake linings from automobiles or similar sources of wind carried asbestos since asbestos contains chromium, incineration of municipal refuse and sewage sludge, exhaust emission from automotive catalytic converters, emissions from cooling towers that use chromium compounds as rust inhibitors, waste waters from electroplating, leather tanning, and textile industries when discharge into surface waters, and solid wastes from chemical manufacture of chromium compounds or from municipal incineration when disposed of improperly in landfill sites. /Total chromium/ [DHHS/ATSDR; Toxicological Profile for Chromium (Draft) p.1 (10/87)].

Particles emitted from coal fired power plants contained 2.3-31 ppm, chromium emitted gases contained 0.22-2.2 mg/cu m. Concns were reduced by fly ash collection to 0.19-6.6 ppm and 0.018-0.5 mg/cu m, respectively. /Total chromium/ [Sullivan RJ; Preliminary Air Poll Survey of Chromium and its Compounds p.1-75 (1969) NAPCA Pub. APTD 69-34 as cited in NAS; Medical and Biological Effects of Environmental Pollutants: Chromium p.15 (1974)].

The burning of wood in fireplaces, campfires, leaf burning, and rubbish incineration contribute chromium to the air. /Total chromium/ [Schroeder HA; API Air Quality Monograph #70-15: Chromium p.1-28 (1970) as cited in NAS; Medical and Biological Effects of Environmental Pollutants: Chromium p.15 (1974)].

Air emissions containing chromium result from the following major industries: paper mills, organic & inorganic petro-chemicals, fertilizers, steel and metal foundries, motor vehicles, glass, cement, asbestos manufacture, textile mills and steam generation power plants. [Dean JG et al; Envir Sci Technol 6: 518-22 (1972) as cited in Nat'l Research Council Canada; Effects of Chromium in the Canadian Envir p.52 (1976) NRCC No.15017].

Wastewater treatment sludge from the production of chrome yellow, orange, and green pigments, chrome oxide green pigments, molybdate orange, zinc yellow, and iron blue pigments, and oven residue from chrome oxide green pigments contain toxic metals including hexavalent

chromium. An est 4300 metric tons of sludge are generated per yr (50-60% of this in 1980 or 2100-2600 lb). These wastes are frequently disposed of in unlined lagoons and landfills or dumped in the open creating a potential for toxic environmental contamination. /Total chromium/ [USEPA; Background Document, Resource Conservation and Recovery Act Subtitle C: Identification and Listing of Hazardous Waste p.188, 202 (1980)].

New York City emits  $4.4 \times 10^8$  g/yr Cr. 43% of the daily Cr in New York City sewer burden and 24% of chromium emission from New York City to vapor are from electroplating wastes, while residential waste and rain water runoff contribute 28% and 9%, respectively. /Total chromium/ [Klein LA et al; J Water Poll Control Fed 46: 2653-62 (1974) as cited in Nat'l Research Council Canada; Effects of Chromium in the Canadian Envir p.58 (1976) NRCC No.15017].

The sources of chromium in waste streams are from its use as a corrosion inhibitor and from dyeing and tanning industries. /Total chromium/ [Brown, K.W., G. B. Evans, Jr., B.D. Frentrup, eds., Hazardous Waste Land Treatment. Boston, MA: Butterworth Publishers, 1983. 252].

#### **Forms/Preparations/Formulations:**

##### Radionuclides:

The symbol for Chromium-51 is  $^{51}\text{Cr}$ , the atomic number is 24, the half-life is 28 days, and X-ray emission is the major form of decay [674].

##### Information from HSDB [940]:

Production & distribution: chromium metal is avail in usa as electrolytic chromium (99.5% Cr), aluminothermic chromium (98.5% Cr) & ductile chromium (99.99% CR). [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. V2 103 (1973)].

Forms available: (1) chromium metal as lumps, granules, or powder; (2) high or low carbon ferro-chromium; (3) single crystals, high purity crystals, or powder run 99.97% Pure. [Sax, N.I. and R.J. Lewis, Sr., eds., Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 280].

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

Solubilities [609]:

Insol (sic, actually relatively insoluble, and dependent upon form) in water [Sax, N.I. and R.J. Lewis, Sr., eds., Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 280].

Vapor Pressure [609]:

1 MM HG @ 1616 DEG C [Sax, N.I. Dangerous Properties of Industrial Materials. 6th ed. New York, NY: Van Nostrand Reinhold, 1984. 790].

Boiling Point [609]:

2642 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 317].

Melting Point [609]:

1900 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 317].

Molecular Weight [609]:

51.996 [Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. B-85].

Density/Specific Gravity [609]:

7.14 [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 317].

Heat of Vaporization [609]:

APPROX 81.7 KCAL/G-ATOM [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 317].

Surface Tension [609]:

1590 + or - 50 mN/m in vacuum at 1950 deg C (Sessile drop method); 1700 + or - 50 mN/m in air at melting point (Dynam drop wt method); 1520 mN/m in air or Helium at 1800 deg C (Sessile drop method) [Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. F-21].

Color/Form [609]:

Steel-gray, lustrous metal; body-centered cubic structure [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 317].

Gray crystals [Sax, N.I. Dangerous Properties of Industrial Materials. 6th ed. New York, NY: Van Nostrand Reinhold, 1984. 790].

Blue-white hard metal [Clayton, G. D. and F. E. Clayton, eds., Patty's Industrial Hygiene and Toxicology: Volume 2A, 2B, 2C: Toxicology. 3rd ed. New York: John Wiley Sons, 1981-1982. 1593].

Odor [609]:

Odorless [Mackison, F. W., R. S. Stricoff, and L. J. Partridge, Jr., eds., NIOSH/OSHA - Occupational Health Guidelines for Chemical Hazards. DHHS(NIOSH) PublicationNo. 81-123 (3 VOLS). Washington, DC: U.S. Government Printing Office, Jan. 1981. 1].

Other Chemical/Physical Properties [609]:

Heat of fusion: 3660 CAL/G MOLE; 62.1 CAL/G [Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. B-218].

Latent heat of fusion: APPROX 3.5 KCAL/G-ATOM; HEAT CAPACITY (25 DEG C): 5.58 CAL/G-ATOM DEG [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 317].

Reactivities and Incompatibilities [609]:

Molten lithium at 180 deg c attacks vanadium, beryllium, or chromium severely. [National Fire Protection Association. Fire Protection Guide on Hazardous Materials. 9th ed. Boston, MA: National Fire Protection Association, 1986.,p. 491M-118].

Violent decomp of hydrogen peroxide (52% by wt or greater) may be caused by contact with ... Chromium ... & Salts. [National Fire Protection Association. Fire Protection Guide on Hazardous Materials. 9th ed. Boston, MA: National Fire Protection Association, 1986.,p. 491M-112].

REACTS WITH DIL HYDROCHLORIC ACID, SULFURIC ACID; NOT WITH NITRIC ACID; ATTACKED BY CAUSTIC ALKALIES & ALKALI CARBONATES. [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 317].

Chromium is attacked vigorously by fused potassium chlorate, producing vivid incandescence. Pyrophoric chromium unites with sulfur dioxide with incandescence. Pyrophoric chromium unites with nitric oxide with incandescence. [National Fire Protection Association. Fire Protection Guide on Hazardous Materials. 9th ed. Boston, MA: National Fire Protection Association, 1986.,p. 491M-66

/Chromium/ contact with /bromine pentafluoride (BrF5)/ at ambient or slightly elevated temp is violent, /with/ ignition

often occurring. [Bretherick, L. Handbook of Reactive Chemical Hazards. 3rd ed. Boston, MA: Butterworths, 1985. 93].

Potentially hazardous incompatibility with strong oxidizers. /Chromium metal and insoluble salts (as Cr)/ [NIOSH. Pocket Guide to Chemical Hazards. 5th Printing/Revision. DHHS (NIOSH) Publ. No. 85-114. Washington, D.C.: U.S. Dept. of Health and Human Services, NIOSH/Supt. of Documents, GPO, Sept. 1985. 82].

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

The residence times of chromium (total) in lake water range from 4.6 to 18 years [927].

Chromium is present in the atmosphere primarily in particulate form [927]. Naturally occurring gaseous forms of chromium are rare. The transport and partitioning of particulate matter in the atmosphere depend largely on particle size and density [927]. Atmospheric particulate matter is deposited on land and water via wet and dry deposition [927]. In the case of chromium, the deposition velocity is 0.5 cm/second [927]. The size and deposition velocity favor dry deposition by inertial impaction [927]. Wet removal of particulate chromium also occurs by rainout within a cloud and washout below a cloud, and acid rain may facilitate removal of acid-soluble chromium compounds from the atmosphere [927]. The wet scavenging ratio (i.e., the concentration of contaminant in precipitation over the concentration in unscavenged air) ranges from 150 to 290 for chromium [927]. The wet deposition ratio increases with particle size and decreases with precipitation intensity [927]. Chromium particles of aerodynamic diameter, less than 20  $\mu\text{m}$  may remain airborne for longer periods of time and be transported for greater distances than larger particles [927]. A maximum of 47% of the total chromium in ferrochrome smelter dust may be bioavailable as indicated by acid/base extraction [927]. About 40% of the bioavailable chromium may exist as chromium(VI), mostly in the form of  $\text{Cr}_2\text{O}_7^{2-}$  or  $\text{CrO}_4^{2-}$  [927]. There are no data in the reviewed literature indicating that chromium particles are transported from the troposphere to the stratosphere [927]. By analogy with the residence time of general particles with mass median diameters similar to that of chromium, the residence time of atmospheric chromium is expected to be less than 10 days [927]. Based on a troposphere to stratosphere turnover time of 30 years, atmospheric particles with a residence time of less than 10 days are not expected to transport from the troposphere to the stratosphere [927]. Since chromium compounds cannot volatilize from water, transport of chromium from water to the atmosphere is not likely, except by transport in windblown sea sprays [927]. Most of the chromium released into water will ultimately be deposited in the sediment [927].

Environmental Fate [940]:

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)].

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: Under normal conditions, chromium(III) and Cr(0) are relatively unreactive in the atmosphere. Cr(VI) in air may react with particulate matter or gaseous pollutants to form Cr(III). However, these atmospheric reactions have not been extensively studied. ... Chromium is removed from air through wet and dry depositions. The total yearly deposition of chromium in urban areas may vary from 0.12 ug/sq m to 3 ug/sq m. In general, urban areas have higher total deposition than rural areas. Chromium concentration in a wet deposition may vary from 0.004 to 0.060 ug/ml and 0.0006 to 0.034 ug/l for urban and rural areas, respectively. The precipitated chromium from the air enters surface water or soil. /Chromium/ [USEPA; Health Assessment Document: Chromium p.3-17 (1984) EPA 600/8-83-014F].

TERRESTRIAL FATE: Uptake is greater from ultrabasic soils by a factor of 5-40 than on calcareous 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)].

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)].

#### Absorption, Distribution and Excretion [940]:

Chromium (Cr) containing aerosol particles with a diam of 2 um are deposited in the upper respiratory tract (nose, pharynx) while smaller particles penetrated to the trachea, bronchial tubes, and alveoli. [Natusch DFS, Wallace JR; Science 186: 695-9 (1974) as cited in Nat'l Research Council Canada; Effects of Chromium in the Canadian Envir p.94 (1976) NRCC No.15017].

In the rat, chromium (Cr) absorbed by the intestines is almost entirely bound to transferrin, the iron-carrying protein. [Hopkins LL, Schwarz K; Biochem Biophys Acta 90: 484-91 (1964) as cited in NAS; Medical and Biological Effects of Environmental Pollutants: Chromium p.37 (1974)].

Chromium (Cr) rapidly accumulates in the testes and then in the epididymes after injection of a tracer dose, thus suggests a possible incorporation of chromium (Cr) into sperm. [Hopkins LL; Amer J Physiol 209: 731-35 (1965) as cited in NAS; Medical and Biological Effects of Environmental Pollutants: Chromium p.39 (1974)].

Chromium is distributed approx equally among human tissues with the exception of lung, which may contain 2-3 times the concn of other tissues. [Seiler, H.G., H. Sigel and A. Sigel, eds., Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 243].

Chromium is normally excreted through the kidneys and urine, with some excretion through the bile and feces; minor routes of excretion incl milk, sweat, hair, and nails. [Seiler, H.G., H. Sigel and A. Sigel, eds., Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 244].

The daily urinary excretion of chromium in 15 female subjects was 0.20 + or - 0.03 ug/l and in 27 male subjects was virtually the same, 0.17 + or - 0.03 ug/l. When chromium intake was supplemented fivefold with chromium chloride, urinary excretion also increased about fivefold. [Anderson RA et al; J Nutr 113 (2): 276-81 (1983) as cited in DHHS/ATSDR; Toxicological Profile for Chromium (Draft) p.48 (10/87)].

In rats, chromium (Cr) (salts) show highest uptake in ovaries, spleen, kidneys, and liver; and chromium (Cr) as glucose tolerance factor shows highest uptake in the liver, uterus, kidneys, and bone. In man, the highest uptake is in the lung

and the chromium (Cr) which accumulates in the liver is concentrated in the nuclei. [NAS; Medical and Biological Effects of Environmental Pollutants: Chromium p.37-39 (1974)].

Nonradioactive and radioactive metal salts were administered intravenously to Sprague Dawley rats. The highest amount of each metal approached the maximum tolerated dose. Cobalt (Co), silver (Ag), and manganese (Mn) were eliminated rapidly. The elimination of 20 to 50 percent of the dosage was observed for copper (Cu), thallium (Tl), bismuth (Bi), lead (Pb), cesium (Cs), gold (Au), zinc (Zn), mercury (Hg), selenium (Se), and chromium (Cr). No substantial elimination rate decline was observed for methyl-mercury, and iron and the decline was small for thallium, cesium, mercury, tin, cobalt, silver, zinc, chromium, and arsenic. Copper, thallium, lead, and zinc were excreted at a slower rate, with 30.6 to 38.3 percent excreted on the first day. The rest of the metals were eliminated slowly by the intestinal route. Cobalt was removed rapidly via urine, while lead, tin, zinc, methyl mercury, silver, iron, manganese, and cadmium were eliminated slowly. Silver, arsenic, manganese, copper, selenium, cadmium, lead, bismuth, and methyl mercury were highly concentrated in bile relative to plasma. Liver and kidney contained the highest concentrations of most metals. Cobalt, cesium, gold, selenium, and chromium were removed predominantly by urine. [Gregus Z, Klaassen CO; Toxicol Appl Pharm 85 (1): 24-38 (1986)].

Hepatic concn of chromium is high in childhood & declines to very low levels after age of 20 yr. /Chromium & inorganic Cr compd/ [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-1985. (Multivolume work).,p. V2 118 (1973)].

Chromium is excreted in urine & feces with the urinary pathway accounting for 80%. Nearly all Cr in urine is present in form of low molecular weight complexes: very little protein bound Cr is excreted. ... Mean 24 hr urinary Cr excretion of 20 young adults was 8.4 U<sub>g</sub> with an avg range of 1.6-21 U<sub>g</sub> ... [National Research Council. Drinking Water & Health Volume 1. Washington, DC: National Academy Press, 1977. 243].

#### Biological Half-Life [940]:

The elimination curve for chromium as measured by whole-body counting has an exponential form. In rats, 3 different components of the curve have been identified with the half-times of 0.5, 5.9, and 83.4 days, respectively. [Friberg, L., Nordberg, G.F., Kessler, E. and Vouk, V.B. (eds). Handbook of the Toxicology of Metals. 2nd ed. Vols I, II.: Amsterdam: Elsevier Science Publishers B.V., 1986.,p. V2 193].

#### Laboratory and/or Field Analyses:

Many methods have been used to monitor for chromium [861,1001,1003,1004,1005,1006]. Separate methods are used for Chromium III and Chromium VI (see separate entries for those elements). EPA methods recommended depend on the application: whether for drinking water [40 CFR Part 141 and 1005,1006], NPDES discharge permits [40 CFR 136 and 1005,1006], CERCLA [861,1005,1006], RCRA [861,1005,1006], or low-detection-limit water-quality based permitting [1001,1003,1004].

For drinking water EPA has recommended method 200.7, 200.8, and 200.9 [1008] as well as EPA 218.2 and SM 304 [893]. For other applications, other methods are recommended [861]. Other agencies (USGS, APHA, ASTM, NOAA, etc. also publish different "standard methods." If one simply wants to know whether or not the concentration exceeds EPA criteria or various low concentration benchmarks for humans, fish, or wildlife, it is not always too clear which "standard method" is optimum, although some might argue that for water, the 1996 EPA methods for trivalent and hexavalent chromium and method 1669 (see details below) should apply.

Determination of chromium has often been by an atomic absorption technique using either direct aspiration into a flame or a furnace [893]. Many of the analytical methods which have been used to detect chromium in environmental samples are the methods approved by federal organizations such as EPA and the National Institute for Occupational Safety and Health (NIOSH) or by groups such as the Association of Official Analytical Chemists (AOAC) and the American Public Health Association (APHA) [927].

Since the valence states are subject to change, tissues are often analyzed for total chromium [609]. During the laboratory digestion of tissue samples, most chromium is changed to the trivalent form [609]. Many labs simply analyze residues for total chromium rather than trying to separate chromium 3 and 6 [609].

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). Atomic absorption (AA) detection limits for water can be as low as 0.001 mg/L (40 CFR Part 141.23, part of the Drinking Water Regulations). Otherwise, the detection limits should usually not exceed the following default ICP detection limit 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).

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, the lab settings were typically fairly clean and the numbers generated by the lab tests are therefore often even more comparable to field "dissolved" values than to

field "total" values (Glen Suter, Oak Ridge National Lab, Personal Communication, 1995). 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 for chromium 3 and chromium 6 [672]:

For example, Chromium +3 conversion for acute and chronic criteria are 0.333 and 0.860, respectively (for example, total recoverable metals acute criteria x 0.333 = dissolved metals acute criteria).

Note: This conversion factor may not hold up for many areas. Both total and dissolved concentrations should be checked at new locations before relying on this conversion factor (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

Although most of the chromium in water binds to dirt and other materials and settles to the bottom, a small amount may dissolve in the water [927]. Soluble chromium compounds can remain in water for years before settling to the bottom [927]. Soluble chromium (VI) may persist in some bodies of water for a long time, but will eventually be reduced to chromium(III) by organic matters or other reducing agents in water [927].

A very small percentage of chromium can be present in water in both soluble and insoluble forms [927]. Soluble chromium generally accounts for a very small percentage of the total chromium [927]. Most of the soluble chromium is present as chromium (VI) and soluble chromium (III) complexes [927]. Less than 0.002% of total chromium in water and sediment in the Amazon and Yukon Rivers was present in a soluble form [927]. In the aquatic phase, chromium (III) occurs mostly as suspended solids adsorbed onto clayish materials, organics, or iron oxide (Fe<sub>2</sub>O<sub>3</sub>) present in water [927]. Approximately 10.5-12.6% of chromium in the aquatic phase of the Amazon and Yukon rivers was in solution, the rest being present in the suspended solid phase [927]. The ratio of suspended to dissolved solid in an organic-rich river in Brazil was 2.1 [927]. Soluble forms and suspended chromium can undergo intramedia transport [927].

#### Filtration and Holding Times:

For water samples for metals, EPA recommends the following (40 CFR Part 136, Appendix C, method 200.7,

1994 edition of CFR Part 40):

1) For samples of "total or total recoverable elements," samples should be acidified to a pH of two or less at the time of collection or as soon as possible thereafter.

2) For determination of dissolved elements, the samples must be filtered through a 0.45 micron membrane filter as soon as soon as practical after collection, using the first 50-100 ml to rinse the filter flask. Acidify the filtrate with nitric acid to a pH of 2 or less. Normally 3 mL of (1+1) of nitric acid per liter should be sufficient to preserve the sample.

3) For determination of suspended elements, the samples must be filtered through a 0.45 micron membrane filter as soon as soon as practical after collection. The filter is then transferred to a suitable container for storage and shipment, with no preservation required.

Sources of potential variation in contaminants data:

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. See also, disclaimers section at the top of this entry. It was recognition that collectors and labs often contaminate samples that led EPA to develop the 1600 series of water protocols for low detection limit applications [1001,1002,1003,1004]. In comparing contaminants data from different labs, different states, and different agencies, one should keep in mind that they are often not very comparable. They may be as different as apples and oranges since:

1) Different Agencies (EPA, USGS, NOAA, and various State Agencies) publish different lab and field protocols. Each of these protocols is different and has typically changed over time.

Note: Even "Standard EPA Methods" which are supposedly widely used by consultants, industry, and academia, have been variable over time and between application category (Drinking Water vs. NPDES, vs. RCRA, vs. CERCLA, vs. Water-Quality Based permits, etc.).

Preservation and other details of various EPA lab and field protocols have changed over the years, just as they have at USGS and various States and other agencies. USGS data from 30 years ago may be different than USGS data today due to differences (drift) in lab and field protocols rather than differences in environmental concentrations.

2) Independent labs and field investigators are not always using "the latest and greatest methods," and it is difficult for them to keep up with all the changes from various agencies in the midst of their "real world" busy lives. Updates are not always convenient to obtain. For example, EPA changes are scattered through various proposed Federal Register Notices, various updates of CFRs, and numerous publications originating in many different parts of EPA and their contractors. The wording is sometimes imprecise and is often inconsistent between EPA methods for different applications.

3) The details of the way one person collects, filters, and acidifies water samples in the field may be different than the way another does it. Sources of potential variation include the following:

A) The protocol phrases "As soon as practical or as soon as possible." Different situations can change the elapsed time considered by the field collector to be "as soon as practical." It may take different amounts of time to get to a safe or otherwise optimum place to filter and/or acidify and cool the samples. In one case precipitation and other changes could be going on in the collection bottle while the bottle is on the way to filtration and acidification. In other cases, the field collector filters and acidifies the samples within minutes. Weather, safety concerns, and many other factors could play a role.

B) Differences in numerous other details of the method used can drastically change the results. Some cold, wet, hurried, or fire ant-bitten collectors might decide that it is not "practical" to filter and acidify quite so immediately in the

field, and may decide the shore, a vehicle, a motel room, or even a remote lab are more "practical" locations. Filtering and acidifying in the field immediately has been thought of as a better option for consistency (see copper and silver entries for examples of what can happen if there is a delay). However, in recent methodology designed to prevent some the contamination and variability listed above, EPA has recently suggested that waiting until the sample arrives at the lab before acidifying is OK [1003].

C) What kind of .45 micron filter was used? The flat plate filters that were used for years tended to filter .45 micron sizes at first and then smaller and smaller sizes as the filtering proceeded and the filter loaded up with particulate matter. As the filter clogged, the openings grew smaller and colloids and smaller diameter matter began to be trapped on the filter. For this reason, both the USGS and EPA 1600 series protocols have gone to tortuous-path capsule filters that tend to filter .45 micron sizes more reliably over time. Example of specifications from EPA method 1669:

Filter-0.45-um, 15-mm diameter or larger, tortuous-path capsule filters, Gelman Supor 12175, or equivalent [1003].

D) "Normally 3 mL of (1+1) of nitric acid per liter should be sufficient to preserve the (water) sample" (40 CFR Part 136, Appendix C, pertaining to ICP analyses using method 200.7, 1994 edition of CFR Part 40). Sometimes it is not, depending on alkalinity and other factors. What field collectors sometimes (often?) do is just use pop tabs of 3 mL of nitric acid and hope for the best rather than checking to see that the acidity has been lowered to below a pH of two. EPA CFR guidelines just call for a pH of below two, whereas samples meant to be "acid soluble" metals call for a pH of 1.5 to 2.0 [25]. See also, various USEPA 1984 to 1985 Ambient Water Quality

Criteria Documents for individual metals.

Note: Some shippers will not accept samples with a pH of less than 1 for standard shipping (John Benham, National Parks Service Personal Communication, 1997).

E) One person might use triple distilled concentrated nitric acid rather than reagent grades of acid to avoid possible contamination in the acid, while another may not. When using very low detection limits, some types of acid may introduce contamination and influence the results. Using a 10% dilution of nitric acid as called for by EPA [1003] is another potential source of contamination, since the dilution water and/or containers may be contaminated. Sometimes people may be incorrectly determining that background concentrations are high due to contamination sources such as these (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

Note: Just using triple distilled nitric acid may not be the total answer to potential contamination. The key issue to be sure that the acid used is free of the metals being analyzed. In guidance for EPA method 1669, the use of "ultrapure nitric acid; or Nitric acid, dilute, trace-metal grade" is specified [1003]. In other EPA guidance, the use of "Nitric acid-concentrated (sp gr 1.41), Seastar or equivalent" is specified [1003].

F) Holding times can strongly influence the results and there can be quite a bit of variation even within EPA recommended 6 month limits (see Silver entry for details). Holding times recommended for EPA for water samples of metals other than mercury or chromium VI have usually been listed as 6 months (Federal Register, Volume 49, No. 209, Friday, October 28, 1984, page 43260). In the 1994 version of the CFR, NPDES holding times for mercury and Chromium VI are the same ones listed in 1984, but no EPA holding times are given for other metals

(40 CFR, Part 136.3, Table 2, page 397, 1994). EPA sources stated this was a typo, that no one else brought it to their attention in the last 3 years, that 6 months is still an operable holding time for "other metals" including this one, and that 6 months is actually an artifact from the days when 6 month composite samples were used for NPDES permits rather than having been originally scientifically derived.

Counterpoint: Although some information suggests that 6 months is probably too long for some contaminants in some scenarios (see silver and copper entries), not all of the information in the literature casts the 6 month metals holding time in such questionable light. In one study, two EPA research chemists found that preservation under certain conditions of drinking water (EPA Method 200.8) metals samples to a pH of less than 2 effectively stabilized the metal concentrations for 6 months. They found that trace metal standards in the 10 to 50 ug/L concentration could be held in 1% nitric acid if a 5% change of concentration was acceptable [1009]. Some metal concentrations changed more than 5% (Zinc up to 24%, Selenium up to 23%) [1009]. Vanadium, Manganese and Arsenic changed up to 5-7% [1009]. In some of the trials, metals were higher after 6 months due to leaching from containers, while in some they were lower [1009]. The changes were nevertheless considered not of great consequence related to drinking water MCLs and EPA method 200.8 [1009]. However, it is not clear that the careful measures utilized (like rechecking to make sure the pH was less than 2, the use of particular kinds of water samples, the use of particular acids, etc.) in this one study replicates what goes on in day to day ("real world") contaminants lab work around the country.

Some EPA sources state that 6 months should be OK if the sample bottle is vigorously shaken and re-acidified in the lab prior to lab analyses, a practice not universally or even particularly commonly done in labs today. 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. Some labs recheck pH, some don't. Some shake, some don't, etc. For drinking water, preservation is considered complete after the sample is held in pH of less than 2 for at least 16 hours [1007].

For many other methods, the minimum holding time in acid is not stated or is different (see various EPA and other Agency methods).

G) If present, air in head space can cause changes in water sample concentrations (Roy Irwin, National Park Service, Personal Communication, based on several discussions with EPA employees and various lab managers in February 1997).

Note: 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).

H) When is the sample shaken in the lab or the field? If the filter is acidified in the field, it will be shaken on the way back to the lab. If lab acidified, how much and when is the sample shaken and then allowed to sit again for various times periods before analyses? Many

methods treat this differently, and what many field collectors and labs actually do before analyzing samples is different as well.

I) If one field filters and acidifies, one often changes metal concentrations and colloidal content compared to samples not treated in this manner. Acidifying effects microbial changes. If one holds the samples a while before filtering and acidifying, the situation changes. In collection bottles, there are potential aging effects: temperature changes, changes in basic water chemistry as oxygen and other dissolved gasses move from the water into the headspace of air at the top, potential aggregation of colloidal materials, precipitation of greater sizes over time, development of bigger and more colloids, and more sorption (Roy Irwin, National Park Service, personal communication, 1997).

4) The guidance of exactly where to take water samples varies between various state and federal protocols. Taking water samples at the surface microlayer tends to increase concentrations of various contaminants including metals. Other areas of the water column tend to produce different concentrations. Large quantities of anthropogenic substances frequently occur in the surface microlayer at concentrations ranging from 100 to 10,000 times greater than those in the water column [593]. These anthropogenic substances can include plastics, tar lumps, PAHs, chlorinated hydrocarbons, as well as lead, copper, zinc, and nickel [593]. Sometimes a perceived trend can be more the result of the details of the sample micro-location rather than real changes in environmental concentrations (Roy Irwin, National Park Service, personal communication, 1997). The new EPA method 1669 mentions the microlayer, and states that one can use a fluoropolymer closing mechanism, threaded onto the bottle, to open and close a certain type of bottle under water, thereby avoiding surface microlayer contamination [1003]. However, even this relatively new EPA method 1669 also gives recommendations for ways to sample directly at the surface, and does not discourage the use of surface samples.

5) Although the above examples are mostly related to water samples, variability in field and lab methods can also greatly impact contaminant concentrations in tissues, soil, and sediments. Sediment samples from different microhabitats in a river (backwater eddy pools vs. attached bars, vs. detached bars, vs. high gradient riffles vs. low gradient riffles, vs. glides, etc.) tend to have drastically different concentrations of metals as well as very different data variances (Andrew Marcus, Montana State University, personal communication, 1995). Thus, data is only optimally comparable if both data collectors were studying the same mix of microhabitats, a stratified sampling approach which would be unusual when comparing random data from different investigators.

6) Just as there are numerous ways to contaminate, store, ship, and handle water samples, so are there different agency protocols and many different ways to handle samples from other media. One investigator may use dry ice in the field, another may bury the samples in a large amount of regular ice immediately after collection in the field, while a third might place samples on top of a small amount of ice in a large ice chest. The speed with which samples are chilled can result in different results not only for concentrations of organics, but also for the different chemical species (forms) of metals (Roy Irwin, National Park Service, personal communication, 1997).

7) In comparing contaminants metals data, soil and sediment contaminant concentrations should usually be (but seldom has been) normalized for grain size, total organic carbon, and/or acid volatile sulfides before biologically-meaningful or trend-meaningful comparisons are possible (Roy Irwin, National Park Service, Personal Communication, 1997).

8) There has been tremendous variability in the precautions various investigators have utilized to avoid sample contamination. Contamination from collecting gear, clothes, collecting vehicles, skin, hair, collector's breath, improper or inadequately cleaned sample containers, and countless other sources must carefully be avoided when using methods

with very low detection limits [1003].

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. 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 to 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 1669 for Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels [1003]:

Note: Method 1669 is applicable to trivalent and hexavalent chromium rather than total chromium. However, when analyzing a low detection limits for total chromium, investigators should consider using the rigorous field precautions recommended in method 1669 for metals in general (Roy Irwin, National Park Service, Personal Communication, 1997).

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].

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.

ATSDR Information:

**BIOLOGICAL MATERIALS** Several methods are available for the analysis of chromium in different biological media [927]. Several other reviews on the subject provide a more detailed description of the available analytical methods [927]. The determination of trace quantities of chromium in biological materials requires special precautionary measures, from the initial sample collection process to the final analytical manipulations of the samples [927]. Contaminations including dust contamination or losses of the samples during collection, transportation, and storage should be avoided [927]. Biological samples collected with stainless steel scalpels, trays, and utensils are unacceptable for chromium analysis [927]. Similarly, contamination or loss arising from sample containers should be avoided [927]. Chromium-containing grinding and homogenizing equipment should not be used for preparation of biological samples [927]. Reagents of the highest purity should be used to avoid contamination [927]. The possible loss of chromium due to volatilization during wet and dry ashing should be minimized [927]. The determination of chromium in most biological samples is difficult because of the matrix interference and the very low concentrations present in these samples [927]. Prior to 1978, numerous erroneous results were reported for the chromium level in urine using electrothermal atomic absorption spectrometry (EAAS) because of the inability of conventional atomic

absorption spectrometry systems to correct for the high nonspecific background absorption [927]. Similarly, the reported serum and plasma chromium concentrations of normal subjects have varied more than 5,000-fold since the early 1950s [927]. The chromium levels in human serum or plasma as reported in the mid-1980s ranged from 0.01 to 0.3 ug/L, and the daily urinary excretion rate of chromium in healthy and nonoccupationally exposed humans is less than 1 ug/day [927]. The four most frequently used methods for determining low levels of chromium in biological samples are neutron activation analysis (NAA), mass spectrometry (MS), graphite spark atomic emission spectrometry (AES), and graphite furnace atomic absorption spectrometry (GFAAS) [927]. Of these four methods, only the GFAAS is readily available in conventional laboratories, and this method is capable of determining chromium levels in biological samples when an appropriate background correction method is used [927]. The problem of developing accurate data for chromium in biological samples is further complicated by the lack of Standard Reference Materials (SRM) [927]. Only recently have chromium certified materials, such as brewer's yeast (SRM-1569), bovine liver (SRM-1577), human serum (SRM-909), urine (SRM-2670), orchard leaves (SRM-1571), spinach leaves (SRM-1570), pine needles (SRM-1575), oyster tissue (SRM-1566), and tomato leaves (SRM-1573) been issued by the National Institute of Standards and Technology (formerly the National Bureau of Standards) [927]. Because of the lack of SRMs, the less recent data should be interpreted with caution, unless the data are verified by interlaboratory studies [927].

Abbreviations: AAS = atomic absorption spectrometry; APDC = ammonium pyrrolidine dithiocarbamate; CEWM = continuum source echelle monochromator wavelength- modulated; EC = electron capture detection; EDTA = ethylenediaminetetraacetic acid; GC = gas chromatography; GFAAS = graphite furnace AAS;  $H_2O_2$  = hydrogen peroxide;  $H_2SO_4$  = sulfuric acid; HCl = hydrochloric acid;  $HClO_4$  = perchloric acid;  $HNO_3$  = nitric acid; ICP-AES = inductively coupled plasma-atomic emission spectrometry;  $Mg(NO_3)_2$  = magnesium nitrate; MIBK = methylisobutyl ketone; MS = mass spectrometry; PIXE = proton-induced X-ray emission spectrometry; XRF = X-ray fluorescence analysis; WM-AES = wavelength- modulated atomic emission spectrometry Another difficulty with the analytical methods used to detect chromium is the ability of the applied analytical method to distinguish between chromium(III) and chromium(VI) [927]. However, in biological samples where chromium is generally present as chromium(III), the choice of a particular method is dictated by several factors including the type of sample, its chromium level, and the scope of the analysis [927]. These factors, in combination with the desired precision

and accuracy and the cost of analysis, should be considered in selecting a particular analytical method [927]. The more recent methods, they are not necessarily the ones most commonly used [927]. A comparison of the various commonly used methods and the methods for the avoidance of contamination during sampling, sample handling, and analysis are provided by Kumpulainen (1984) [927].

ENVIRONMENTAL SAMPLES: Chromium may be present in both the trivalent and hexavalent oxidation states in most ambient environmental and occupational samples, and sometimes the distinction between soluble and insoluble forms of chromium(VI) is necessary [927]. The quantification of soluble and insoluble chromium is done by determining chromium concentrations in aqueous filtered and unfiltered samples [927]. However, soluble chromium(VI) may be reduced to chromium(III) on filtering media, particularly at low concentrations and under acidic conditions [927]. Teflon filter and alkaline solution are most suitable to prevent this reduction [927]. Routine analytical methods are not available that can quantify the concentration of both chromium(VI) and chromium(III) in air samples when present at a total concentration of 1 ug/cubic m, although two methods can determine chromium(VI) concentrations alone in air at a minimum detection limit of 0.1 ng/m<sup>3</sup> for a 20m<sup>3</sup> sample [927]. The three commonly used methods that have the best sensitivity for chromium detection in air are GFAAS, instrumental neutron activation analysis (INAA), and graphite spark atomic emission spectrometry [927]. Measurements of low levels of chromium concentrations in water have been made by specialized methods, such as inductively coupled plasma mass spectrometry (ICP-MS), capillary column gas chromatography (HRGC) of chelated chromium with electron capture detection (ECD), and electrothermal vaporization inductively coupled plasma mass spectrometry [927]. 1989; Malinski et al [927]. 1988; Schaller and Neeb 1987) [927]. A method using high performance liquid chromatography interfaced with direct current plasma emission spectrometer has been used for the determination of chromium(III) and chromium(VI) in water samples [927]. As in the case of biological samples, contamination and chromium loss in environmental samples during sample collection, storage, and pretreatment should be avoided [927]. Chromium loss from aqueous samples due to adsorption on storage containers should be avoided by using polyethylene or similar containers and acidifying the solution to the proper pH [927]. The preferred methods for digestion of environmental samples have been discussed [927].

Analytic Laboratory Methods [609]:

It can be shown 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)].