ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

BERYLLIUM 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 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 uniformed or be caught by surprise by potentially important information. They are in a better position if they can say: "I knew about that data, assessed it based on the following quality assurance criteria, and decided not to use it for this application." This is especially true for users near the end of long decision processes, such as hazardous site cleanups, lengthy ecological risk assessments, or complex natural resource damage assessments.

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

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

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

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

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

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

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

on the internet or NTIS: 1998).

Beryllium (Be, CAS number 7440-41-7)

NOTE: This entry contains information on both elemental beryllium and various beryllium compounds.

Brief Introduction:

Br.Class: General Introduction and Classification Information:

Beryllium is a rare chemical element, one of the alkaline-earth metals in Group IIA of the periodic table [294]. Beryllium is a hard, grayish element [944].

Chemically, beryllium differs markedly from the other alkaline-earth metals in that it forms compounds that are more covalent than ionic [294]. Beryllium's properties are similar to those of aluminum and magnesium, except that its melting point, about 1,278 deg C, is high for a light metal [294].

The element does occur as a chemical component of certain rocks, coal and oil, soil, and volcanic dust [944]. Appalachian coal can contain 2.5 ppm beryllium [494]. Two kinds of mineral rocks, betrandite and beryl, are mined commercially for the recovery of beryllium. Beryllium is also present in a variety of compounds. There are two types of beryllium compounds: those that dissolve in water and those that do not [944].

Beryllium is a carcinogenic priority pollutant [302,446]. Beryllium is listed by the Environmental Protection Agency as one of 129 priority pollutants [58], and is considered one of the 14 most noxious heavy metals [83].

Beryllium is listed among the 25 hazardous substances thought to pose the most significant potential threat to human health at priority superfund sites [93]. Beryllium is a toxic pollutant designated pursuant to section 307(a)(1) of the Clean Water Act and is subject to effluent limitations (40 CFR 401.15, 7/1/88) [366].

Br.Haz: General Hazard/Toxicity Summary:

Potential Impacts to Fish, Wildlife, Invertebrates, and Plants:

Beryllium may be taken up by plants at levels that result in yield reduction; phytotoxicity of beryllium is caused by the inhibition of enzyme activity. The growth inhibiting effects usually recognized in higher plants are reduced as the pH is raised above 6.0, and it has been proposed that the decreased toxicity is caused by beryllium precipitation at high pH levels. The response of plants to beryllium in soil did not cause a yield decrease in neutral pH soils but substantially decreased plant yields in quartz soils (Brown, K.W., G. B. Evans, Jr., B.D. Frentrup, eds., Hazardous Waste Land Treatment. Boston, MA: Butterworth Publishers, 1983. 244) [940].

All beryllium compounds are potentially harmful or toxic [83]. However, the probability of beryllium occurring at significantly toxic levels in ambient natural waters is minimal [375]. This is partly because of physical chemical and fate factors:

> Most beryllium is expected to be present either in the sorbed state in suspended matter or in the sediment rather than in a dissolved form in most natural waters [944]. Empirical data indicate that, even in polluted rivers where the concentration of complexing agents is high, dissolved beryllium levels are very low [944]. The chloride and nitrate salts of beryllium are very soluble in water, the sulfate is only moderately so, and the carbonate and hydroxide are virtually insoluble in cold water [375]. Even in the heavily polluted Rhine and Main rivers in Germany, the concentrations were below 0.02 ug/l (see W.Typical Section below for details).

However, in those cases in which it is elevated in water, beryllium is extremely toxic to warmwater fish in soft water [944]. The degree of toxicity decreases with increasing water hardness [944]. For many metals, alkalinity is sometimes even a more important co-factor for toxicity than hardness (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

There are several studies regarding death in animals after acute inhalation exposure to beryllium compounds [944].

Potential Impacts to Humans:

The lung appears to be the main target organ for beryllium toxicity in humans and animals [494,944]. Human impacts of beryllium include berylliosis, a severe lung inflammation caused by occupational exposure [173].

Beryllium can enter waters in effluents from certain metallurgical plants, but the inhalation of beryllium-containing fumes and dust originating from processing and fabrication operations poses the most serious health hazard to humans [302]. ` Acute exposure to high concentrations of the more soluble compounds of beryllium can cause chemical pneumonitis, the symptoms of which include cough, substernal burning, shortness of breath. anorexia, and increasing fatigue [944].

Beryllium can provoke immune responses, and immune status appears to influence development of pulmonary berylliosis in beryllium exposed subjects [494].

The toxicity of beryllium could be accounted for through its effect on lysosomes with release of cell destroying enzymes (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. 1547) [940].

A comprehensive toxicological profile for beryllium and its compounds, especially as it relates to human health, is available from ATSDR [944]. Due to lack of time, important highlights from this ATSDR document have not yet been completely incorporated into this entry.

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

EPA 1996 IRIS database information [893]:

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

Classification: B2; probable human carcinogen [893].

BASIS: Beryllium has been shown to induce lung cancer via inhalation in rats and monkeys and to induce osteosarcomas in rabbits via intravenous or intramedullary injection. Human epidemiology studies are considered to be inadequate [893].

HUMAN CARCINOGENICITY DATA: Inadequate. Reported increases, while apparently associated with exposure, did not take a variety of possible confounding factors into account [893].

Animal carcinogenicity data: Sufficient. Based on the evidence for induction of tumors by a variety of beryllium compounds in male and female monkeys and in several strains of rats of both sexes, via inhalation and intratracheal instillation, and the induction of osteosarcomas in rabbits by intravenous or intramedullary injection in multiple studies [893].

The International Agency for Research on Cancer has determined that beryllium and beryllium compounds are probably carcinogenic to humans.

Classification of carcinogenicity: 1) evidence in humans: limited; 2) evidence in animals: sufficient; Overall summary evaluation of carcinogenic risk to humans is group 2A: The agent is probably carcinogenic to humans. /from table, beryllium and beryllium compounds/ (IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-1985. (Multivolume work).,p. S7 127, 1987)[366].

Beryllium has been shown to be a carcinogen in rats and rabbits [22,168]. Some beryllium compounds are carcinogenic in animals exposed via inhalation. Rats exposed to 0.035 mg/m3 as beryllium sulfate for 180 days had increased lung cancer rates, compared to controls [944].

Beryllium metal was administered by intratracheal instillation to the rat causing lung cancer, adeno and squamous cell carcinomas (Groth DH et al; Environ Res 21: 63, 1980, as cited in Kuschner M; The Carcinogenicity of Beryllium, Environ Health Perspect 40: 101-5, 1981)[366].

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

Beryllium has been shown to be teratogenic in snails, and to cause developmental problems in salamanders [22,168].

No studies were located regarding developmental, reproductive, or genotoxic effects in human or animals after inhalation exposure to beryllium or its compounds [944].

Beryllium did inhibit replication of DNA in regenerating rat livers but did not become attached to DNA; it perhaps interfered with nucleic acid metabolism on transcriptional level (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. 110) [940].

Beryllium crosses the placenta only to a small extent (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 190, 1980)[366].

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

Little data is available, but early speculation was that the potential for bioaccumulation or bioconcentration of beryllium may be low for the following biota: mammals, birds, fish, mosses, lichens, mollusks, crustacea, lower animals, higher plants and algae [83].

Beryllium enters the air, water, and soil as a result of natural and human activities. Emissions from burning coal and oil increase beryllium levels in air. Beryllium enters waterways from the wearing away of rocks and soil. Most of the man-made beryllium that enters waterways comes when industry dumps wastewater and when beryllium dust in the air from industrial activities settles over water [944].

Plants take up beryllium from soil, groundwater, and air pollution [83]. Animals take up beryllium from contaminated water and food [83].

A major portion of beryllium in soil does not dissolve in water but remains bound to soil, so it is not very likely to move deeper into the ground and enter groundwater [944]. Possible reactions of beryllium in soil are hydrolysis of soluble salts, anion exchange reaction by which one salt is converted to another, and complexation reactions with ligands present in the soil (such as humic substances). Reactions of beryllium in soil are likely to be responsive to pH [944]. Due to fate factors, the probability of having toxic levels of beryllium in water is usually not great (see Br.Haz section above).

In the environment, chemical reactions can change the water-soluble beryllium compounds into insoluble forms. In some cases, water-insoluble beryllium compounds can change to soluble forms [944].

Synonyms/Substance Identification:

Beryllium-9 [944]
Glucinium [944]

Glucinum [944]
Beryllium metallic [944]

Molecular formula [944]:
Be

Associated Chemicals or Topics (Includes Transformation Products):

Various beryllium compounds. No other information found.

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

W.Low (Water Concentrations Considered Low):

The average beryllium concentration in Australian rainwater ranged from 0.05-0.08 ug/L [944].

The concentration of several metals in drinking waters from two New York City municipalities was measured [944]. Beryllium was not detected in any samples at a detection limit of 10 ug/L [944].

W.High (Water Concentrations Considered High):

Beryllium has been detected in treated waste waters from nonferrous metal manufacturing industries at a maximum concentration of 170 ug/L and at a mean concentration of 30 ug/L in treated waste water from paint and ink formulation industries [944].

W.Typical (Water Concentrations Considered Typical):

In the absence of a special source, river waters usually have very low or non-detectable concentrations of beryllium [190].

Typical Ocean Concentrations: EPA 1981: 0.0000006 mg/l [83].

Typical Freshwater Concentrations: EPA 1981: 0.001 mg/l [83].

The median total beryllium concentration in the Great Lakes ranged from < 4 to 120 ng/L [944].

An analysis of 1,577 drinking water samples revealed that beryllium was detected in 5.4% of the samples and that concentrations ranged from 0.01 to 1.22 mg/l with a mean value of 0.19 ug/l (Kopp JF, Kroner RC; Fed Water Pollut Control Admin, 1967, as cited in USEPA; Ambient Water Quality Criteria Doc: Beryllium p.C-1, 1980, EPA 440/5-80-024] [366,944].

In Australian river waters, the total beryllium concentration ranged from less than 10 to 120 ng/L, with an average of 10-30 ng/L [944].

Analysis of surface, ground, and rain waters have shown that beryllium concentrations are well below 1.0 ug/l. The maximum beryllium concentration in 20 rain water samples and 56 river water samples (from 5 different Australian rivers) was 0.18 ug/l. Even in the heavily polluted Rhine and Main rivers in Germany, the concentrations were below 0.02 ug/l (EPA; Ambient Water Quality Criteria Doc: Beryllium p.A-1, 1980, EPA 440/5-80-024) [366].

Using the data of ambient, lake, and stream stations monitored by the U.S.Geological Survey and EPA's STORET database from ≈1960 to 1988, the geometric mean concentration of total beryllium in U.S..surface water was estimated to be 70 ng/L [944].

The total beryllium concentrations in various freshwaters ranged from 10 to 1000 ng/L [944]

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):

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

For CAS 7440-41-7 (Beryllium, the benchmarks in ug/L are:

NATIONAL AMBIENT WATER QUALITY CRITERION - ACUTE: No information found.

NATIONAL AMBIENT WATER QUALITY CRITERION - CHRONIC: No information found.

SECONDARY ACUTE VALUE: 271

SECONDARY CHRONIC VALUE: 5.09

ESTIMATED LOWEST CHRONIC VALUE - FISH: 57

LOWEST CHRONIC VALUE - DAPHNIDS: 5.3

LOWEST CHRONIC VALUE - NON-DAPHNID INVERTEBRATES: No information found.

LOWEST CHRONIC VALUE - AQUATIC PLANTS: 100,000

ESTIMATED LOWEST TEST EC20 - FISH: 148

LOWEST TEST EC20 - DAPHNIDS: 3.8

SENSITIVE SPECIES TEST EC20: No information found.

POPULATION EC20: 21

EPA 1996 Ambient Water Quality Criteria for Aquatic Organisms [893]:

Acute Freshwater Criterion: 1.3E+2 ug/L LEC [893]. Explanation: Freshwater Acute Criteria: Insufficient data to develop criteria [893].

Older published value was the same: Lowest Observed Effect Level: 130 ug/L [446].

Chronic Freshwater Criteria: 5.3E+0 ug/L LEC [893]. Freshwater Chronic Criteria: Insufficient data to develop criteria [893].

Older published value was the same: Lowest Observed Effect Level: 5.3 ug/L [446].

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

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

Discussion: The values that are indicated as "LEC" are not criteria, but are the lowest effect levels found in the literature. LECs are given when the minimum data required to derive water quality criteria are not available. Hardness has a substantial effect on acute toxicity [893].

Marine Acute Criteria: None Published [446,893].

Marine Chronic Criteria: None Published [446,893].

Criteria Federal Register Notice Number: 45 FR 79326, see also: USEPA; Ambient Water Quality Criteria Doc: Beryllium p.A-1 (1980) EPA 440/5-80-024 [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].

Other Concern Levels for Water Concentrations:

For soft fresh water the criterion for the protection of aquatic life is established at 0.011 mg/L [375]. The criterion for the protection of aquatic life in hard fresh water is established at 1.10 mg/L. As can be seen from these criteria, beryllium is considerably (100 times) more toxic in soft water than in hard water [375].

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 7440-41-7, Beryllium, the benchmark is 0.5 mg/L (porewater or groundwater).

Irrigation Water Concern Level:

Because of its toxicity in nutrient solutions in acid soils, the criterion for beryllium in irrigation waters is 0.50 mg/L for use on neutral to alkaline fine-textured soils and 0.10 mg/L for use on all other soils [302].

An irrigation water concentration limit of 100 ug/L has been suggested for use on all soils [190].

Growth of freshwater green alga Chlorella was inhibited at 100,000 ug/L [22].

W.Invertebrates (Water Concentrations vs. Invertebrates):

The 48 hour LC50s for Daphnia magna were 2,500 to 7900 ug/L [22].

W.Fish (Water Concentrations vs. Fish):

Tlm Pimephales promelas (fathead minnow) 150 ug/l/96 hr (soft water) /Conditions of bioassay not specified/ (Schwitzgebel K et al; Trace Element Discharge from Coal-fired Power Plants Vol II: 146, 1975, as cited in Nat'l Research Council Canada; Data Sheets on Selected Toxic Elements p.15, 1982, NRCC No. 19252)[366].

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

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

For CAS 7440-41-7 (Beryllium, as beryllium sulfate), the benchmarks are:

SPECIES	WATER CONCENTRATION (ppm)
Rat (test species)	0.00000
Short-tailed Shrew	8.48300
Little Brown Bat	14.66200
White-footed Mouse	5.48200
Meadow Vole	9.59500
Cottontail Rabbit	4.54700

Mink	4.71500
Red Fox	3.36500
Whitetail Deer	1.88300

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

EPA 1995 Region 9 PRG Tap Water Preliminary Remediation Goal: 1.6E-02 ug/L [868].

EPA 1996 IRIS database information [893]:

Maximum Contaminant Level Goal: 0 mg/L [893].

Status/Year: Proposed 1990 Econ/Tech?: No, does not consider economic or technical feasibility Reference: 55 FR 30370 (07/25/90) [893].

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

Discussion: The proposed MCLG for beryllium is zero based on the evidence of carcinogenic potential (B2). [893].

Maximum Contaminant Level (MCL): 0.001 mg/L [893].

Status/Year: Proposed 1990 Econ/Tech?: Yes, does consider economic or technical feasibility Reference: 55 FR 30370 (07/25/90) [893].

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

Discussion: The MCL is based on 5x the MDL, which is associated with a maximum lifetime individual risk of 1E-4. [893].

Drinking Water Concentrations at Specified Risk Levels:

Risk Level Concentration E-4 (1 in 10,000) 8.3E-1 ug/liter E-5 (1 in 100,000) 8.3E-2 ug/liter E-6 (1 in 1,000,000) 8.3E-3 ug/liter [893].

Ambient Water Quality Criteria for Human

Health [893]:

Water & Fish: 6.8E-3 ug/liter [893].

Older reference: Human Health for Carcinogens (risk of one additional case in 1 million, 1E-06): Published Criteria for Water and Organisms: 0.0037 ug/L [446,689]. Older IRIS Recalculated (7/93) Criteria for Water and Organisms: 0.0076 ug/L [689].

Fish Only: 1.17E-1 ug/liter [893].

Reference: 45 FR 79318 (11/28/80); Quality Criteria for Water, EPA 440/5-86-001 (5/87)

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

Discussion: For the maximum protection from the potential carcinogenic properties of this chemical, the ambient water concentration should be zero. However, zero may not be attainable at this time, so the recommended criterion represent a E-6 estimated incremental increase of cancer risk over a lifetime. [893].

Older Published Criteria for Organisms Only: 0.0641 ug/L [446,689]. Older IRIS Recalculated (9/90 to 93) Criteria for Organisms Only: 0.131 [446,689].

State Water Quality Standards for Drinking Water:

Arizona	0.007 ug/L [940,944]
Kansas	0.13 ug/L [944]
NH	0.004 ug/L [944]
MN	0.08 ug/l [940].

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

Beryllium enters waterways from the wearing away of rocks and soil [944]. Most of the man-made beryllium that enters waterways comes when industry dumps waste water and when beryllium dust in the air from industrial activities settles over water [944].

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).

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):

Analyses of sewage sludges from 50 publicly owned treatment works by the U.S. Environmental Protection Agency (1985): The mean concentration of beryllium was 1.2 ppm (dry weight) [347].

Analyses of 74 Missouri sewage sludges (1985): The mean for beryllium was 0.6 ppm (dry weight), the range was 0.2-3.4 ppm (dry weight) [347].

Sed.Typical (Sediment Concentrations Considered Typical):

Beryllium levels in the sediments of Lake Pontchartrain, Louisiana, were 0.05 - 0.5 mg/kg (dry weight). Sediments in the Detroit River and west basin of Lake Erie were 0.1 to 3.8 mg/kg (dry weight) [944].

Sediment concentrations of beryllium in Buffalo Lake National Refuge ranged from 0.19 mg/kg dry weight at site SW to 1.2 mg/kg dry weight at site SPI [401].

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

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

No information found.

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):

Upon reaching water and soil, beryllium will probably be retained in an insoluble form in sediment and soil and will be generally immobile [944]. Although chemical reactions may transform one beryllium compound into another, beryllium cannot be degraded by environmental reactions [944]. However, the data regarding transformation reactions of beryllium in water and soil are limited [944].

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):

Analyses of sewage sludges from 50 publicly owned treatment works by the U.S. Environmental Protection Agency (1985): The mean concentration of beryllium was 1.2 ppm (dry weight) [347].

Analyses of 74 Missouri sewage sludges (1985): The mean for beryllium was 0.6 ppm (dry weight), the range was 0.2-3.4 ppm (dry weight) [347].

Soil.Typical (Soil Concentrations Considered Typical):

Average concentration in soil from 6 states was 0.6 mg/kg [944].

Averages and ranges of concentrations of elements in soils and other surficial materials in the United States (1971): The mean concentration of beryllium was 1 ppm, the range was <1-7 ppm [347].

Soil concn generally range from 0.1-40 ppm, with the average around 6 ppm. (Brown, K.W., G. B. Evans, Jr., B.D. Frentrup, eds., Hazardous Waste Land Treatment. Boston, MA: Butterworth Publishers, 1983. 244) [940].

Beryllium is a rare element: its concentration in the Earth's crust is approximately 6 ppm, and no rich deposits of it exist [294]. The average beryllium concentration in the Earth's crust is ≈2.8-5.0 mg/kg [944]. Igneous Rocks (Earth's Crust) Concentrations not Considered Elevated: EPA 1981: 2.8 mg/kg dry weight [83].

The concentration range of beryllium in 15 soil samples obtained from six states in the United States was 0.13-0.88 mg/kg, with an average concentration of 0.4 mg/kg [944]. 1978) [944]. The beryllium concentration in an English peat bog ranged from 0.06 to 0.3 mg/kg [944].

EPA 1981: 6.0 mg/kg dry weight not considered elevated [83].

Various geochemical surveys have found typical beryllium concentrations in soil to range from 0.01 to 40.0 mg/kg, with a median value of 0.3 mg/kg. Using USGS data, the mean concentration of beryllium in U.S. soil was estimated to be 0.6 mg/kg [944].

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):

The 1987 soil (clean up) criteria given by the New Jersey Department of Environmental Protection for beryllium is 1 mg/kg dry weight [347,386].

Suggested safe applications of beryllium to Missouri soils without further investigations (1988): The maximum cumulative addition of beryllium is 112 kg/ha [347].

Soil.Plants (Soil Concentrations vs. Plants):

Levels of beryllium (ppm dry weight) considered phytotoxic: 10 (Vienna), 10 (Warsaw), 10 (Warsaw) [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 7440-41-7 (BERYLLIUM), the benchmark is 10 mg/kg in soil (Kloke, 1979).

See also: discussion of soil beryllium vs. pH vs. plants in Br.Hazard section above.

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 = 0.1 mg/kg for ingestion pathway [952].

SSL = 1300 mg/kg for inhalation pathway [952].

SSL = 3 to 63 mg/kg for protection from migration to groundwater at 1 to 20 Dilution-Attenuation Factor (DAF) [952].

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

Residential Soil: 0.14 mg/kg wet wt.
Industrial Soil: 1.1 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:

180 mg/Kg dry weight [903].

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

The possible reactions of beryllium in soil are hydrolysis of soluble salts, anion exchange reaction by which one salt is converted to another (e.g., beryllium sulfate may be converted to beryllium carbonate), and complexation reactions with ligands present in soil (e.g., humic substances) [944]. Reactions of beryllium in soil are likely to be responsive to pH [944]. However, experimental evidence of any such reactions in soil was not located in the literature [944]. Data suggesting the biotransformation of beryllium or its compounds in soil were not located [944].

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:

Beryllium concentrations in both raw carrots and field corn grown in the U.S. were < 25 ug/kg fresh (wet) weight (detection limit 25 ug/kg) [944].

Plant Concentrations [366]:

In birch, aspen, and willow, beryllium content may rise as high as 3 mg/kg. Potatoes contain 0.17 mg/kg dry substance, tomatoes 0.24 mg/kg and head lettuce 0.33 mg/kg. /Total beryllium/ [Seiler, H.G., H. Sigel and A. Sigel, eds., Handbook on the Toxicity of Inorganic Compounds. New York, NY:

Marcel Dekker, Inc. 1988. 112].

Beryllium in root, stem, and leaf tissues of tobacco (Nicotiana tabacum L Md-609) plants grown in McMurtrey's nutrient solution with addition of 0.3, 1.0 and 3.0 mg/l Be were determined by gas chromatography-mass spectrometric analysis using m/l 246 of beryllium trifluoroacetylacetonate chelates. The method was sensitive to about 4 pg of Be. The majority of Be was associated with tobacco roots (0.3, 1.0 and 3.0 mg/l of Be were added to the solution were associated with 374, 427 and 4280 ug Be/g dry wt of tissue, respectively; leaves were associated with 2.14, 2.36 and 81.4 ug Be/g dry wt tissue respectively. [Kosak-Channing L; Plant Sci 46 (3): 175-80 (1986)].

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:

The following text is quoted from the Buffalo Lake National Wildlife Refuge report [201] for reference comparison with values from other areas:

> Tissue Concentration Results: Of the 17 tissue samples analyzed for metals, beryllium was found above detection limits (0.043 mg/kg dry weight) only in one tiger salamander sample from site PL (0.13 mg/kg dry weight or 0.017 mg/kg wet weight) and in two whole-body crayfish samples from site SR (0.11 and 0.19 mg/kg dry weight).

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 beryllium concentration in bottom fish (English sole) caught in Commencement Bay, Tacoma, Washington, was 6 ug/kg [944].

The following text is quoted from the Trinity River Report [201] for reference comparison with values from other areas:

> Beryllium was found above detection limits (0.002 mg/kg) in 56 of 77 Trinity River samples analyzed for metals.
>
> Maximum Levels: The three highest concentrations of beryllium (0.033 to 0.052 mg/kg) were in mosquitofish downstream of Dallas, as were 6 of the 8 highest levels.
>
> Gradient Monitoring Levels: Beryllium showed a tendency to increase from upstream to downstream in mosquitofish. A group of mosquitofish samples from sites just downstream of Dallas had significantly higher concentrations of beryllium than a group of mosquitofish samples from sites upstream of Fort Worth or Dallas.

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):

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

For CAS 7440-41-7, Beryllium, as beryllium sulfate, the benchmarks are:

SPECIES	NOAEL (mg/kg/day)	FOOD CONCENTRATION (ppm)
Rat (test species)	0.66000	0.00000
Short-tailed Shrew	1.86600	3.11000
Little Brown Bat	2.34600	7.03800
White-footed Mouse	1.64500	10.64200
Meadow Vole	1.30800	11.51400
Cottontail Rabbit	0.44000	2.22500
Mink	0.46700	3.40700
Red Fox	0.28400	2.84100
Whitetail Deer	0.12300	4.00300

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

See also Tis.Invertebrates, C) above for tissue concentrations in a salamander.

Milk Concentrations [366]:

According to studies on cows with radioactive beryllium, less than 0.002% Of injected activity was recovered in milk. Biological half-life in milk was 19 hr. /Total beryllium/ [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. 102].

Beryllium level /reported/ in milk, 0.02 ppm in ash. /Total beryllium/ [Mechan WR, Smythe LE; Environ Sci Technol 1: 839 (1967) as cited in USEPA; Ambient Water Quality Criteria Doc: Beryllium p.C-1 (1980) EPA 440/5-80-024].

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

Beryllium concentrations in both raw carrots and field corn grown in the U.S. were < 25 ug/kg fresh (wet) weight (detection limit 25 ug/kg) [944]. Several foodstuffs from New South Wales, Australia, were analyzed, and the following average beryllium concentrations were found (in ug/kg fresh weight): beans (0.065); cabbage (0.234); hen eggs yolk and whites (0.061); milk (0.166); mushrooms (1.58); edible nuts (0.21-0.52); tomatoes (0.21); crabs (15.4-26.2); fish fillets (0.16-1.48); oyster flesh (0.6-2.0); and scallops (0.34) [944].

The following beryllium concentrations (ug/kg dry weight) were reported in West German food samples: polished rice (80); toasted bread (120); potatoes (170); tomatoes (240); and green head lettuce (330) (Reeves 1986) [944]. The reported beryllium concentrations (ug/kg dry weight) in crops from Egypt were as follows: eggplant (370); potatoes (300); green pepper (400); kidney bean (2,500); garden pea (430); vegetable marrow (400); pear (400); lettuce (600); dill (6 [944].

Food Survey Results [366]:

Beryllium concentrations (dry weight) of 0.08 mg/kg in polished rice, 0.12 mg/kg in toasted bread, 0.17 mg/kg in potatoes, 0.24 mg/kg in tomatoes, and 0.33 mg/kg in head lettuce. /Total beryllium/ [Petzow G, Zorn H; Chemlker Vig 98: 236 (1974) as cited in USEPA; Ambient Water Quality Criteria Doc: Beryllium p.C-1 (1980) EPA 440/5-80-024].

Beryllium levels (ppm in ash) for different foodstuffs were: beans, 0.01; cabbage, 0.05; hen eggs (yolk) 0.01; milk, 0.02; mushrooms, 0.12; nuts, 0.01- 0.47; tomatos, 0.02; and baker's yeast, 0.02. /Total beryllium/ [Mechan WR, Smythe LE; Environ Sci Technol 1: 839 (1967) as cited in USEPA; Ambient Water Quality Criteria Doc: Beryllium p.C-1 (1980) EPA 440/5-80-024].

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):

Crit. Dose: 0.54 mg/kg-day [Study 1 NOAEL(adj)] UF: 100 MF: 1 [893].

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

Cancer Slope Factor: 4.3E+0 per mg/(kg/day) [893,952].

Unit Risk: 1.2E-4 per ug/liter Extrapolation Method: Linearized multistage procedure, extra risk [893,952].

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

Body Burdens [366]:

Humans: total body burden: 36 ug Beryllium; 24 ug Beryllium in soft tissue. /Total beryllium/ [Nat'l Research Council Canada; Data Sheets on Selected Toxic Elements p.15 (1982) NRCC No. 19252].

Humans: Kidney; 0.2 ug beryllium/kg: liver; 1.6 ug beryllium/kg: muscle; 0.75 ug beryllium/kg: bone; 3.0 ug beryllium/kg: hair; 6.0-20.0 ug beryllium/kg /Total beryllium/ [Bowen HJM; The Environmental Chemistry of the Elements 103 (1982) as cited in [Nat'l Research Council Canada; Data Sheets On Selected Toxic Elements p.15 (1982) NRCC No. 19252].

Human: blood: 0.01 ug beryllium/l /Total beryllium/ [Bow HJM; The Environmental Chemistry of the Elements 105 (1980) as cited in [Nat'l Research Council Canada; Data Sheets on Selected Toxic Elements p.15 (1982) NRCC No. 19252].

Humans: lung: 1x10+2 to 1x10+5 ug beryllium/l: blood: 0.02-3.0 ug beryllium/l: urine: 0.02-3.0 ug beryllium/l /Total beryllium/ [Reeves AL; Beryllium In Toxicology of Metals Vol 2 93 (1977) EPA-600/1-77-022 as cited in Nat'l Research Council Canada; Data Sheets on Selected Toxic Elements p.15 (1982) NRCC No. 19252].

The soft tissue burden of an adult is likely to be less than 20 ug and the skeletal burden about 30 ug. /Total beryllium/ [Meehan WR, Smythe LE; Environ Sci Technol 1: 839-44 (1967) as cited in USEPA; Health Assessment Document for Beryllium p.4-6 (1987) EPA 600/8-84/0267].

Tis.Misc. (Other Tissue Information):

Beryllium toxicity to plants is severe [951].

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

Plants take up beryllium from soil, groundwater, and air pollution [83]. Animals take up beryllium from contaminated water and food [83]. Beryllium is not expected to bioconcentrate in aquatic animals [944].

Bioconcentration of beryllium in fish to high levels is not likely due to the low uptake of beryllium from water by aquatic animals [944]. A measured bioconcentration factor (BCF) of 19 was reported for beryllium in bluegill fish [944]. Other investigators have reported a BCF of 100 for freshwater and marine plants, invertebrates, and fish [944]. According to Kenaga (1980), chemicals with BCFs of less than 1000 will not bioaccumulate significantly in aquatic organisms [944]. It is possible that bottom-feeding crustaceans, such as clams and oysters, could accumulate beryllium from sediment and show higher bioconcentration than freshwater fish [944]. Comparisons of the beryllium levels in biota and surface sediments from Lake Pontchartrain, Louisiana, indicated similar, but somewhat lower, beryllium concentrations in biota [944]. The BCFs for beryllium in bottom-feeding animals could not be estimated from this investigation since the authors did not report the beryllium concentration in water [944]. No evidence for significant biomagnification of beryllium within food chains was found [944].

Little data is available, but early speculation was that the potential for bioaccumulation or bioconcentration of beryllium may be low for the following biota: mammals, birds, fish, mosses, lichens, mollusks, crustacea, lower animals, higher plants and algae [83]. The best potential mediums for biological monitoring appear may include clams and higher plants [83]. Irwin found mosquitofish to be acceptable for gradient monitoring of beryllium [201].

Bioconcentration of beryllium in fish to high levels is not likely due to the low uptake of beryllium from water by aquatic animals. A measured bioconcentration factor (BCF) of 19 was reported for beryllium in bluegill fish [944]. Other investigators have reported a BCF of 100 for freshwater and marine plants, invertebrates, and fish [944].

In marine organisms, beryllium has been reported to be concentrated as much as 1000 times the ambient concentration [224,302].

Biological Half-Life [366]:

Inhaled beryllium has initial pulmonary half-life of about 0.5-6 Months, but a particulate residuum tends to remain in lungs for long periods. Some accumulation in tracheobronchial lymph nodes. Pulmonary deposition & clearance may come to an equilibrium. [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. 95].

The biological half-life is long because absorption in the lung takes place rather slowly and a proportion of beryllium or its cmpd is stored in the liver and skeleton. /Beryllium/ [Seiler, H.G., H. Sigel and A. Sigel, eds., Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 110].

An accidental exposure of 25 persons to beryllium dust was used to follow up trace analysis and clin parameters over a period of 10 mo. The Be clearance shows a biol half-time in the range of 2-8 wk. [Zorn H et al; Toxicol Environ Chem 12 (3-4): 163-71 (1986)].

Interactions:

Beryllium is considerably (100 times) more toxic in soft water than in hard water [375]. See also: discussion of soil beryllium vs. pH vs. plants in Br.Hazard section above.

Information from HSDB [366]:

Concomitant exposure to acid (hydrofluoric) fumes may increase toxic effect. [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 166].

Uses/Sources:

Beryllium occurs as a chemical component in certain rocks, coal and oil, soils, and volcanic dust. Two kinds of mineral rocks, betrandite and beryl, are mined commercially to recover beryllium [944].

Most of the beryllium that is mined is converted into alloys (mixtures of metals) [944]. The addition of traces of beryllium to alloys can greatly increase their corrosion resistance [294]. But the cost of beryllium, which is about 200 times that of aluminum, restricts its applications to a few special ones, such as in computer components, gyroscopes, and space technology. Beryllium is important in nuclear-reactor technology because it is an excellent neutron reflector and moderator. For this reason, and because of its strength and great resistance to heat, beryllium is employed as a cladding material for nuclear fuel elements. The most important beryllium compound is beryllium oxide, BeO. It is used as a base material in ceramics and in special types of glass; in fluorescent tubes; and in nuclear reactors [294].

Primary sources of beryllium to a river are typically atmospheric fallout from the burning of coal, soil erosion, industrial discharges, and sewage treatment plants [22]. Floodplain-located landfills containing discarded pieces of high technology equipment might also be a potential source. Beryllium also can enter waters in effluents from certain metallurgical plants [302].

Beryllium is probably emitted into the atmosphere as beryllium oxide (BeO) [944]. The atmospheric emission of beryllium during ore-crushing processes is likely to occur in the form of BeO because the two commonly used beryllium ores, beryl and bertrandite, both contain BeO [944]. The atmospheric emission of beryllium during thermal processes, such as coal and refuse combustion, is also likely to produce BeO in the stack emission [944]. As is the case with other metallic compounds, BeO cannot be destroyed; however, it could be transformed from one form to another [944]. It is not known whether BeO in air will react with sulfur or nitrogen oxides to produce beryllium sulfate or nitrate

[944]. If such conversion occurs, the removal of beryllium from the atmosphere by wet deposition will be accelerated since both beryllium sulfate and nitrate are water-soluble [944]. Experimental data that would substantiate the possibility of any reaction of BeO in air were not located [944].

Natural Sources [366]:

Estimates of abundance in earth's crust vary from 2 to 10 ppm. Natural isotopes: 9 (100%); radioactive isotopes (mass numbers): 6-8; 10-12. ... Found in phenacite, chrysoberyl ... Precious forms of beryl: emerald, aquamarine. /Total beryllium/ [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 166].

Beryllium is concentrated in silicate minerals relative to sulfides. In common crystalline rocks, the element is enriched in the feldspar minerals relative to ferromagnesium minerals and apparently replace the silicon ion; 85-95% of the total crystal beryllium may be bound in the feldspar structures. ... The greatest known concentrations of beryllium are found in certain pegmatite bodies, where crystals of beryl account for a few percent of the total pegmatite volume, and may be found in several of the strata of zoned dykes. The element is sometimes concentrated in hydrothermal veins, and some granitic rocks contain sufficient amounts to permit the crystallization of small amounts of beryl. /Total beryllium/ [Beus AA; Geochemistry 5: 432 (1966) as cited in USEPA; Ambient Water Quality Criteria Doc: Beryllium p.A-1 (1980) EPA 440/5-80-024].

Certain fossil fuels contain beryllium cmpd, accounting for the presence of beryllium in some community air samples and tissues of city residents. /TOTAL BERYLLIUM/ [Hamilton, A., and H. L. Hardy. Industrial Toxicology. 3rd ed. Acton, Mass.: Publishing Sciences Group, Inc., 1974. 57].

Artificial Sources [366]:

Ceramic artists can be exposed to many hazardous materials, generally related to dry clays, glazes and kiln use. Glazes can contain lead, antimony, arsenic, barium, beryllium, boron, chromium, cobalt, cadmium, copper, vanadium and other materials which all have potential toxic effects. /Total beryllium/ [Hart C; J Environ Health 49 (5): 282-6 (1987)].

Beryllium enters the environment principally from coal combustion. Be contents in the ashes from a Czechoslovakian power plant were determined (coarse (> 20 mm) and fine (2.0 to 0.2 mm) fraction from dump, and fine (0.2 mm) fraction from electrostatic precipitators). Acidic and alkali aqueous extracts of these ashes contained various concentrations of Be (1 to 17% of total concentrations). Wastewater showed 3.15 and 3.4 ug Be/l. Thus, secondary long term beryllium pollution emerges from the slag and ash dumps. [Kubiznakova J; Water Air Soil Pollut 34 (4): 363-68 (1987)].

Other Environmental Concentrations [366]:

In cigarettes beryllium levels of 0.5-0.7 ug/cigarette were analyzed with 4.5-10% escaping with the smoke. [Seiler, H.G., H. Sigel and A. Sigel, eds., Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 112].

Forms/Preparations/Formulations:

Radionuclides:

The symbol for Beryllium-7 is 7Be, the atomic number is 4, the half-life is 53.3 days, and X-ray emission is the major form of decay [674].

The symbol for Beryllium-10 is 10Be, the atomic number is 4, the half-life is 1,600,000 years, and beta emission is the major form of decay [674].

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

Solubilities [944]:

Water: Insoluble (sic, actually "relatively insoluble").
Organic solvents: Soluble in dilute acid and alkali.

Vapor pressure [944]: 1 mmHg (1,520 degrees C).

Density [944]: 1.846 g/cm3.

Boiling point [944]: 2,970 degrees C.

Melting point:

1,287 - 1,292 degrees C [944].
1,278 degrees C [294].

Atomic weight [294]: 9.0122.

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

The likely reaction for beryllium in water is chemical speciation by which one species is converted to another [944]. One such possible reaction in water is hydrolysis [944]. Soluble beryllium salts in water are hydrolyzed to form relatively insoluble beryllium hydroxide, which would have a low solubility in the pH range of most natural waters [944]. Complexation with hydroxide ions to form soluble polynuclear hydroxide complexes is another possible reaction, although the pH range necessary for this reaction is probably not available in most natural waters [944]. This is substantiated by empirical data that indicate that, even in polluted rivers where the concentration of complexing agents is high, dissolved beryllium levels are very low [944].

The transport of beryllium from the atmosphere to terrestrial and aquatic surfaces occurs through wet and dry deposition [944]. The dry deposition rate of aerosol particles is a function of particle aerodynamic size, windspeed, and surface roughness [944].

Some beryllium may also be present in the sediment as a result of formation and subsequent precipitation of insoluble complexes [944]. A high percentage of beryllium is expected to have low mobility in water due to association in the sediment, although at a high water pH, formation of water- soluble complexes with hydroxide ions may increase the solubility and mobility of beryllium [944]. The estimated residence time of beryllium in ocean water (before it is removed from the aquatic phase by sedimentation or other removal processes) is about a few hundred years [944]. No evidence was found to substantiate that biomethylation or any other environmental process results in the volatilization of beryllium into the atmosphere from water or soil [944].

In most types of soil, beryllium is expected to be tightly adsorbed because it displaces divalent cations that share common sorption sites [944]. Due to its geochemical similarity to aluminum, beryllium may be expected to adsorb onto clay surfaces at low pHs, and it may remain precipitated as insoluble complexes at higher pHs [944]. Therefore, beryllium is expected to have limited mobility in soil [944]. At high soil pH, the mobility of beryllium in soil may increase as a result of formation of soluble polynuclear hydroxide complexes [944]. However, beryllium was not detected (detection limit not stated) in soil water or groundwater in Fresno, California [944]. Beryllium is, therefore, not likely to be found in a soluble state in most soils, and it may not leach through soil to contaminate most groundwaters [944].

Biological Half-Life [940]:

1. Inhaled beryllium has initial pulmonary half-life of about 0.5-6 Months, but a particulate residuum tends to remain in lungs for long periods. ... Some accumulation in tracheobronchial lymph nodes. Pulmonary deposition & clearance may come to an equilibrium. [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. 95].

2. The biological half-life is long because absorption in the lung takes place rather slowly and a proportion of beryllium or its cmpd is stored in the liver and skeleton. /Beryllium/ [Seiler, H.G., H. Sigel and A. Sigel, eds., Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc. 1988. 110].

3. An accidental exposure of 25 persons to beryllium dust was used to follow up trace analysis and clin parameters over a period of 10 mo. The Be clearance shows a biol half-time in the range of 2-8 wk. [Zorn H et al; Toxicol Environ Chem 12 (3-4): 163-71 (1986)].

Absorption, Distribution and Excretion [940]:

1. Storage of absorbed beryllium takes place in bones ... There is some retention of a transient nature by liver, kidney and lung. ... [Browning, E. Toxicity of Industrial Metals. 2nd ed. New York: Appleton-Century-Crofts, 1969. 69].

2. Tissue content of persons suffering from acute ... Poisoning is ... Higher than that shown by chronic cases. In five chronic cases ... Amt varied up to 0.99 Ug/100 g in the lung, up to 0.68 In liver, up to 10 in lymph nodes, up to 0.7 In spleen. ... [Browning, E. Toxicity of Industrial Metals. 2nd ed. New York: Appleton-Century-Crofts, 1969. 71].

3. Animal studies show that be moves out of lung and may later return there. All studies indicate beryllium is so poorly absorbed through gut that ingestion is not a hazard. [Hamilton, A., and H. L. Hardy. Industrial Toxicology. 3rd ed. Acton, Mass.: Publishing Sciences Group, Inc., 1974. 56].

4. Prolonged excretion can follow even slight exposure; beryllium has been detected in urine up to 10 yr after cessation of exposure. [Browning, E. Toxicity of Industrial Metals. 2nd ed. New York: Appleton-Century-Crofts, 1969. 70].

5. Organ distribution of beryllium appears ... Dose dependent: 2.5 Hr after ... IV injection to rats, small doses ... Taken up preferentially in skeleton, & higher doses ... Preferentially in liver. Beryllium was later mobilized from liver & transferred to skeleton. Beryllium is excreted partly in urine. Because of colloidal binding in plasma, beryllium does not cross glomerular membrane, & it is excreted via the tubules. Proportion of intratracheally injected beryllium excreted in urine was 20-69%. [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 182 (1980)].

6. Beryllium crosses the placenta only to a small extent. [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 190 (1980)].

7. Storage of beryllium in all major tissue sites is of long duration, particularly in the pulmonary lymph nodes & bone. Hence elimination of beryllium from the body is extremely

slow, & the last 5% requiring many months or years to disappear completely from these latter two sites. [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. 1546].

8. Absorption of ingested beryllium probably only occurs in the acidic milieu of the stomach, where it is in the ionized form, but passes through the intestinal tract as precipitated phosphate. [Doull, J., C.D.Klassen, and M.D. Amdur, eds., Casarett and Doull's Toxicology. 3rd ed., New York: Macmillan Co., Inc., 1986. 591].

9. Absorption from the digestive tract is slight (above 0.006% Of that ingested) ... [National Research Council. Drinking Water & Health Volume 1. Washington, DC: National Academy Press, 1977. 233].

10. The ultimate site of accumulation of beryllium is the skeleton. [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. V1 24 (1980)].

11. .Not much /beryllium/ is absorbed from the GI tract. ... Sol salts are ppt by reaction with proteins in alimentary tract ... Beryllium forms insol phosphates in intestine ... Rendering any phosphate going into soln in intestinal fluids or ... Liberated by enzymatic hydrolysis of phosphoric esters unavailable for absorption. [Browning, E. Toxicity of Industrial Metals. 2nd ed. New York: Appleton-Century-Crofts, 1969. 69].

12. Intratracheally deposited beryllium also is retained in the lung and part of it is deposited in the bone. ... Parenterally administered beryllium is stored ultimately in the bone. [Venugopal, B. and T.D. Luckey. Metal Toxicity in Mammals, 2. New York: Plenum Press, 1978. 45].

13. Excretion of unabsorbed dietary beryllium is fecal in rats & other animals; 96% of a single dietary dose is excreted within 24 hr & the rest slowly over a period of 4-5 wk. [Venugopal, B. and T.D. Luckey. Metal Toxicity in Mammals, 2. New York: Plenum Press, 1978. 45].

14. Parenterally injected & inhaled beryllium salts, as well as beryllium absorbed from digestive tract, are excreted very slowly if at all; less than 1% is excreted in urine & feces within 1st 24 hr, but fecal excretion is persistent in barely detectable amt & is extended over a long period. [Venugopal, B. and T.D. Luckey. Metal Toxicity in Mammals, 2. New York: Plenum Press, 1978. 46].

15. There seems to be no homeostatic regulatory mechanism for

beryllium; beryllium accumulates in mammalian tissue with age. [Venugopal, B. and T.D. Luckey. Metal Toxicity in Mammals, 2. New York: Plenum Press, 1978. 46].

16. Circulating beryllium was carried to all tissues, & analyses following admin normally yielded measurable levels in most organs. On short-term basis (2.5 Hr after iv injection) organ distribution was dose dependent, favoring skeleton for smaller doses ... & Liver for larger doses ... Part of absorbed beryllium /following iv injection/ estimated at 20-69%, was excreted in urine. Plasma beryllium did not pass the glomerulus & mechanism of excretion was tubular, with some damage inflicted upon tubular epithelium in the course of secretion. [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. 102].

17. In humans exposed to about 3 ug be/cu m inhaled air, excretion is mainly urinary & amt excreted is determined by the solubility of the beryllium salt. There is prolonged excretion in urine, with beryllium detected in urine for 10 yr following exposure ... /Beryllium/ [Venugopal, B. and T.D. Luckey. Metal Toxicity in Mammals, 2. New York: Plenum Press, 1978. 46].

18. It has been established that hilar nodes and lung of city dwellers and coal miners contain beryllium in detectable amt. [Hamilton, A., and H. L. Hardy. Industrial Toxicology. 3rd ed. Acton, Mass.: Publishing Sciences Group, Inc., 1974. 57].

19. The solubility of two industrial forms of beryllium, ie, particles of metal powder and particles of hot pressed beryllium, was investigated using in vivo and in vitro models. In the in vivo model, baboons and rats were used and were injected via the trachea with amounts of beryllium equivalent to 100, 500 and 1000 fold the maximum permissible concentration (MPC) recommended by the USA Occupational Safety and Health Administration. In vivo experiments showed that in both species the daily beryllium solubility rates were about 5-6 for metal particles and that in rats the daily beryllium solubility rate was about 5 during the 10 months of the experiment with baboons, urinary excretion of beryllium was proportional to the amount administered. With regard to results for the in vitro models, the outcome of the acellular dissolution test using a serum stimulant was not consistent with the in vivo results, though a cellular model using cultured macrophages showed the same trends in the dissolution rates for the two forms of beryllium as those observed in vivo. This result suggests that a cellular rather than an acellular dissolution model would be better at predicting solubility of beryllium compounds in the lungs. [Andre S et al; Hum Toxicol 6 (3): 233-40 (1987) [940].

Laboratory and/or Field Analyses:

Many methods have been used to monitor for beryllium [861,944]. EPA methods recommended depend on the application: whether for drinking water [40 CFR Part 141], NPDES discharge permits [40 CFR 136], CERCLA [861,1005,1006], RCRA [861,1005,1006]. The new EPA low-detection-limit water-quality based permitting 1600 series methods do not seem to apply directly to beryllium [1001,1003,1004]. 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, some of the field precautions recommended by EPA method 1669 [1003] should apply.

Low concentration criteria or benchmarks may require relatively rigorous methods, while routine applications may require only 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). Many national and state standards or benchmarks are below 1 ppb for drinking water. Otherwise, the detection limits should usually not exceed the following default concentrations often recommended by the Fish and Wildlife Service and the National Park Service: Detection limits 0.10 ppm dry weight in tissues, 0.20 ppm in sediments and soils, 0.0005 ppm to 0.01 ug/L in water (Roy Irwin, National Park Service, Personal Communication, 1996). In cases where benchmark comparisons require lower detection limits, graphite furnace atomic absorption methods are available to achieve: 0.01 ug/L in liquids and 1 ppb in solids [944]. EPA recommended Atomic absorption (AA) detection limits for water can be as low as 0.00002 mg/L (EPA method 200.9 as described in 40 CFR Part 141.23, part of the Drinking Water Regulations).

However, normal background concentrations in soils, sediments, and tissues of certain areas may be so high that the lowest detection limits are unnecessary (see Soil, Sediment, and Tissue sections above).

EPA 1996 IRIS database drinking water information [893]:

> Monitoring Requirements
>
> Ground water systems every 3 years; surface water systems annually; will allow monitoring at up to 10-year intervals after the system completes 3 rounds of sampling at <50% of the MCL.
>
> Analytical Methods
>
> Atomic absorption/furnace technique (EPA 210.2; ASTM D-3645; SM 304); inductively-coupled plasma (EPA 200.7; SM 305); ICP mass spectrometry (EPA 200.8): PQL= 0.001 mg/L.

Filtration and Holding Times:

For ICP water samples for metals, EPA recommends the following (40 CFR Part 136, Appendix C, pertaining to ICP analyses using 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. 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 (see additional discussion in the disclaimers section at the top of this entry). 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 guidance for EPA method 1638, 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 in insure data comparability or method validity. Even volunteer monitoring programs are now strongly encouraged to develop and use quality assurance project plans [1015,1017].

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

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

Detailed Methods Information for Beryllium from ATSDR [944]:

BIOLOGICAL MATERIALS Methods used for the analysis of beryllium in biological materials. Although the beryllium level in urine may be informative of the current exposure level, it is not useful as a diagnostic criterion [944]. However, the level of beryllium in blood/serum/plasma is predictive of the intensity of current exposure from certain beryllium compounds [944]. Flame atomic absorption spectroscopy or atomic emission spectroscopy is not sensitive enough for measuring the beryllium concentration in body fluids and tissues [944]. The determination of beryllium levels in these matrices requires elimination of severe matrix interference [944]. In particular, Ca^{+2} and Mg^{+2} enhance and CI^- and CIO_4^- cause severe suppression of beryllium absorption in atomic spectroscopy [944]. Electrothermal or graphite furnace atomic absorption spectroscopy with background correction (deuterium or Zeeman effect background corrector) is the commonly used method, and it has the sensitivity and accuracy to determine beryllium content in body fluids and tissues [944]. To avoid sample contamination, stainless steel needles should be avoided for the collection of whole blood samples [944]. Certain polyethylene sample collection tubes with added heparin as an anticoagulant may contaminate whole blood samples [944]. A time-consuming gas chromatographic method to detect beryllium in whole blood down to a concentration level of 0.02 ug/mL is available [944]. A relatively recent technique called the Laser Ion Mass Analyzer (LIMA) uses a laser beam to ionize elements in a small section of tissue and detects ions including beryllium by a time-of-flight mass spectrometer [944]. Standard reference materials (SRMs) are useful to determine the accuracy of an analytical method [944]. A standard reference urine (SRM 2,670) with a certified beryllium concentration is available from National Institute of Standards and Technology [944]. 1989) [944]. 6.2

ENVIRONMENTAL SAMPLES: Environmental samples analyzed by atomic absorption spectroscopy and gas chromatography require pretreatment to remove interfering substances and increase sensitivity [944]. At high concentrations (500 mg/kg), aluminum and silicon interfere with beryllium analysis by atomic absorption spectroscopy [944]. Separation of these elements is achieved by chelation and extraction with an organic solvent [944]. A method using laser spark spectroscopy has been used for the direct determination of trace quantities of airborne beryllium collected on filters [944]. The following SRMs for beryllium in environmental samples are available from the National Institute of Standards and Technology: coal, SRM 1,632; fly ash, SRM 1,633; trace elements in water, SRM 1,643; orchard leaves, SRM 1,571; and filter media, SRM 2,676 [944]. 1982; Epstein et al [944]. 1978; Gladney and Owens 1976) [944]. In addition, SRMs MESS-1 and BCSS-1 for beryllium in sediments are available from the National Research Council of Canada [944].

See also: EMMI EPA listing of lab methods [861].