ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

NICKEL ENTRY

July 1, 1997

COMPILERS/EDITORS:

ROY J. IRWIN, NATIONAL PARK SERVICE

WITH ASSISTANCE FROM COLORADO STATE UNIVERSITY

STUDENT ASSISTANT CONTAMINANTS SPECIALISTS:

MARK VAN MOUWERIK

LYNETTE STEVENS

MARION DUBLER SEESE

WENDY BASHAM

NATIONAL PARK SERVICE

WATER RESOURCES DIVISIONS, WATER OPERATIONS BRANCH

1201 Oakridge Drive, Suite 250

FORT COLLINS, COLORADO 80525

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Like a library or many 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 without 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 or summaries 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).

Nickel (Ni, CAS number 7440-02-0)

Brief Introduction:

Br.Class: General Introduction and Classification Information:

Nickel is a hard, silvery metal heavily used in industrial purposes which is also abundant in the earth's crust [190]. It has properties that make it very desirable for combining with other metals to form mixtures called alloys. Some of the metals that nickel is alloyed with are iron, copper, chromium, and zinc. Most nickel is used to make stainless steel. Nickel also combines with other substances such as chlorine, sulfur, and oxygen to form nickel compounds. Many of these compounds dissolve fairly easily in water and have a characteristic green color. Nickel and its compounds have no characteristic odor or taste [949].

Nickel occurs naturally in the earth's crust, is found in all soils, and is also emitted from volcanos [949]. Nickel is released into the atmosphere during nickel mining and by industries that convert scrap or new nickel into alloys or nickel compounds or by industries that use nickel and its compounds. These industries may also discharge nickel in waste water. Nickel is also released into the atmosphere by oil-burning power plants, coal-burning power plants, and trash incinerators [949].

Divalent nickel is the primary aqueous form [190]. Nickel 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, 7/1/87) [940].

Nickel is listed by the Environmental Protection Agency as one of 129 priority pollutants [58], and is considered to be one of the 14 most noxious heavy metals [83]. Nickel is also listed among the 25 hazardous substances thought to pose the most significant potential threat to human health at priority superfund sites [93].

Br.Haz: General Hazard/Toxicity Summary:

Nickel carbonyl is among the most toxic nickel compounds [83]. In studies of subsurface agricultural irrigation drainage waters of the San Joaquin Valley of California, nickel was determined to be a "substance of concern, additional data needed" [445].

Mixtures of nickel, copper, and zinc produced additive toxicity effects on rainbow trout [57].

Although hardness is used in water quality criteria

equations (see W.General section below), for many metals, alkalinity is sometimes a more important co-factor for toxicity than hardness (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

Low absorption from the GI tract causes nickel compounds to be essentially nontoxic after ingestion (Leonard A/ et al; Mutat Res 87 (1): 1, 1981) [940].

The organs which are affected by exposure to nickel, metal and soluble compounds (as Ni) are nasal cavities, lung, skin (NIOSH. Pocket Guide to Chemical Hazards. 5th Printing/Revision. DHHS, NIOSH Publ. No. 85-114. Washington, D.C.: U.S. Dept. of Health and Human Services,NIOSH/Supt. of Documents, GPO, Sept., 1985,. 173) [940].

The toxicity to humans of nickel or nickel salts through oral intake is low. Nickel salts exert their action mainly by gastrointestinal irritation and not by inherent toxicity. (National Research Council. Drinking Water and Health. Volume 3. Washington, DC: National Academy Press, 1980. 348) [940].

Toxic to humans as dust or powder (Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 818) [940].

A comprehensive toxicological profile for nickel, especially as it relates to human health, is available from ATSDR [949]. Due to lack of time, important highlights from this ATSDR document have not yet been completely incorporated into this entry.

Environment Canada has prepared the comprehensive Priority Substances List Assessment Report for nickel and its compounds [950]. Due to lack of time, no information from this Environment Canada document has yet been incorporated into this entry. EPA has a free and informative (several page) health advisory on this metal, available through the Office of Drinking Water, EPA, Washington, D.C. or through NTIS.

Bionecessity [940]:

> Nickel deficiency; also leads to iron deficiency; impairs iron absorption. [Schnegg A, Kirchgessner M; Nut Metabol 19: 268 (1975)].
>
> There is a growing body of literature that establishes an essential role for nickel, ... in experimental animals. One key criteria for element essentiality, existence of specific nickel-

deficiency syndromes, is reasonably satisfied for nickel. Various researchers have shown different systemic lesions in various animals deprived of dietary nickel. Nickel deprivation has an effect on body weight, reproductive capability, viability of offspring, and induction of anemia through reduced absorption of iron. Jack bean urease (and possibly rumen microbial urease) has been shown to be a nickel-requiring enzyme. In animals, there is a homeostatic mechanism for regulating the metabolism of nickel and the existence of nickel proteins. [USEPA; Health Assessment Document: Nickel p.9 (1983) EPA-600/8-83-012].

Nickel deficiency has been reported in birds; deficiency is unlikely in humans taking a conventional diet; the margin between required & toxic concentration is wide. [Reynolds, J.E.F., Prasad, A.B. (eds.) Martindale-The Extra Pharmacopoeia. 28th ed. London: The Pharmaceutical Press, 1982. 47].

Pathological signs of nickel deficiency have been produced in chickens, rats and swine. Retarded growth, anemia, and decreasing enzyme activities are among the signs seen in rat. [Friberg, L., Nordberg, G.F., Kessler, E. and Vouk, V.B. (eds). Handbook of the Toxicology of Metals. 2nd ed. Vols I, II.: Amsterdam: Elsevier Science Publishers B.V., 1986.,p. V2 471].

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

EPA 1996 IRIS database information [893]:

Soluble salts: The U.S. EPA has not evaluated soluble salts of nickel, as a class of compounds, for potential human carcinogenicity [893]. However, for soluble salts (no CAS number), the available data indicate a hazard ranking of low and a weight-of-evidence classification of C, which corresponds to an RQ of 100 pounds.

Nickel in general (CAS number 7440-02-0): not listed in 1996 IRIS [893]. However, nickel in general, CAS 7440-02-0 is listed as a class A carcinogen in another 1996 EPA document [952].

Nickel refinery dust (No CAS number):

Classification as to human carcinogenicity weight-of-evidence classification:

Classification: A; human carcinogen

BASIS: Human data in which exposure to nickel refinery dust caused lung and nasal tumors in sulfide nickel matte refinery workers in several epidemiologic studies in different countries, and on animal data in which carcinomas were produced in rats by inhalation and injection

Nickel carbonyl CAS: 13463-39-3 [893]:

Classification as to human carcinogenicity weight-of-evidence classification:

Classification: B2; probable human carcinogen

BASIS: Based upon the observation of pulmonary carcinomas and malignant tumors at various sites in rats administered nickel carbonyl by inhalation and intravenous injection, respectively. Nickel administered as nickel carbonyl binds to DNA.

HUMAN CARCINOGENICITY DATA: Inadequate.

ANIMAL CARCINOGENICITY DATA: Sufficient. Nickel carbonyl administered by inhalation has been found to be carcinogenic in animals in the lung

For modeling purposes, EPA 1995 Region 3 Risk based concentration (RBC) table states that nickel in general was not considered a carcinogen but that nickel subsulfide as well as nickel refinery dust were considered carcinogens [903]. For modeling purposes, EPA 1995 Region 9 PRG publication states that nickel soluble salts were not considered a carcinogen but that nickel subsulfide as well as nickel refinery dust were considered carcinogens [868]. These assignments were for modeling purposes only.

Little information is available on the effects of nickel body burdens on fish and wildlife, but experimental doses of nickel have induced cancer in rats, guinea pigs, and rabbits [35]. Some salts of this element are carcinogenic [168]. Nickel is present in asbestos and may play a role in asbestos carcinogenicity [35].

Although water soluble nickel salts have not been shown to initiate carcinogenesis in rodents, the soluble nickel

salts are evidently effective as cancer promoters following initiation of tumorigenesis by aromatic hydrocarbons and nitrosoamines [940].

Growing evidence suggest that the nickel(III)/nickel(II) redox couple facilitates oxygen free radical reactions, which may represent one of the molecular mechanisms for carcinogenicity of nickel compounds [940].

There is sufficient evidence in humans for the carcinogenicity of nickel sulfate, and of the combinations of nickel sulfides and oxides encountered in the nickel refining industry. There is inadequate evidence in humans for the carcinogenicity of metallic nickel and nickel alloys. There is sufficient evidence in experimental animals for the carcinogenicity of metallic nickel, nickel monoxides, nickel hydroxides and crystalline nickel sulfides. There is limited evidence in experimental animals for the carcinogenicity of nickel alloys, nickelocene, nickel carbonyl, nickel salts, nickel arsenides, nickel antimonide, nickel selenides and nickel telluride. There is inadequate evidence in experimental animals for the carcinogenicity of nickel trioxide, amorphous nickel sulfide and nickel titanate. The Working Group made the overall evaluation on nickel compounds as a group on the basis of the combined results of epidemiological studies, carcinogenicity studies in experimental animals, and several types of other relevant data, supported by the underlying concept that nickel compounds can generate nickel ions at critical sites in their target cells. Overall evaluation: Nickel compounds are carcinogenic to humans (Group 1). Metallic nickel is possibly carcinogenic to humans (Group 2B). [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. 49 410 (1990) [940].

Notice of Intended Change (first notice appeared in 1992-93 edition): A1. A1 = Confirmed human carcinogen. /Nickel, elemental, insoluble and soluble compounds, as Ni/ (American Conference of Governmental Industrial Hygienists. Threshold Limit Values for Chemical Substances and Physical Agents and Biological ExposureIndices for 1994-1995. Cincinnati, OH: ACGIH, 1994. 37) [940].

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

Study results indicate that nickel is a developmental toxicant in animals, but it is not known whether occupational or environmental exposure to nickel could

result in developmental effects in humans [949].

Prenatal effects of nickel result from direct insults to the mammalian embryo as well as from indirect ones through maternal damage. Nickel may upset the hormonal balance of the mother and can impair the development of the preimplantation embryo. The metal can cross the feto-maternal barrier and enter the fetus. In addition to an increase in prenatal and neonatal mortality, nickel can produce different types of malformations in the surviving embryos but its teratogenic action seems to be delayed, probably as a result of retarded transfer via the placenta. No definite conclusions can be reached, at the present time, as to whether the embryotoxicity and fetal toxicity of nickel is eventually related to its mutagenic properties. Nickel alters macromolecular synthesis but no convincing evidence has been provided of its ability to produce gene mutations or structural chromosome aberrations in mammalian cells (Leonard A, Jacquet P; IARC Sci Publ 53: 277-91, 1984) [940].

Nickel was given in drinking water to rats for 7 mo before pregnancy and during pregnancy and some incr of preimplantation mortality was found. Some cases of malformed fetuses was noted. (Shepard, T.H. Catalog of Teratogenic Agents. 5th ed. Baltimore, MD: The Johns Hopkins University Press, 1986. 408) [940].

Animal data indicate that nickel is a reproductive toxicant in animals, but it is not known whether occupational or environmental exposure to nickel could result in reproductive effects in humans [949].

Nickel was reported to affect male and female reproductive capacity [494,940].

Growing evidence suggest that the nickel(III)/nickel(II) redox couple facilitates oxygen free radical reactions, which may represent one of the molecular mechanisms for genotoxicity of nickel compounds [940].

The in vitro and in vivo genotoxicity data indicate that nickel is genotoxic. Nickel has been reported to interact with DNA, resulting in crosslinks and strand breaks [949].

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

Nickel occurs in soil and is often bound up in soil or sediment particles [949]. The concentration of nickel in unpolluted waters is typically low [949, see also

W.Typical section below]. Although most lab analyses for nickel are for total nickel, the hazard presented by nickel, and its exact fate characteristics depend upon chemical speciation [949].

Nickel is moderately accumulated in many food chain organisms (see Bio.Detail section below for detail). The bioaccumulation or bioconcentration of nickel is moderate for the following biota: mammals, birds, and fish; while the potential for bioaccumulation appears to be highest for mollusks, crustacea, lower animals, mosses, lichens, algae, and higher plants [83].

Nickel may be released to the environment from the stacks of large furnaces used to make alloys, or from power plants, and trash incinerators. The nickel that comes out of the stacks of the power plants is attached to small particles of dust that settle to the ground or are taken out of the air in rain. It will usually take many days for nickel to be removed from the air. If the nickel is attached to very small particles, removal can take longer than a month. Nickel cannot be destroyed in the environment. It can only move around, change its form, or become attached to or separated from particles. Most nickel will end up in the soil or sediment where it is strongly attached to particles containing iron or manganese. Under acidic conditions, nickel is more mobile in soil and may seep into groundwater. Nickel does not appear to concentrate in fish. Two recent studies indicate that it does not accumulate in plants growing on land that has been treated with nickel-containing sludge or in small animals living on that land [949].

According to NIOSH, the toxicologically important routes of entry for nickel, metal & soluble compounds in humans (as Ni) are inhalation, skin absorption, ingestion, and skin and/or eye contact [940].

Synonyms/Substance Identification:

CI 77775 [940]
NI 0901-S [940]
RANEY NICKEL [940]
RCH 55/5 [940]
NI 0901-S (HARSHAW) [940]
NICHEL (ITALIAN) [940]
NICKEL SPONGE [940]
NP 2 [940]
NP-2 [940]
RANEY ALLOY [940]
NI 270 [940]
NI 4303T [940]

NI-4303T [940]
NICKEL 270 [940]
Nickel 200 [940]
Nickel 201 [940]
Nickel 205 [940]
Nickel 207 [940]
Carbonyl nickel powder [940]

Molecular Formula [940]:
Ni

Associated Chemicals or Topics (Includes Transformation Products):

Often found associated with cobalt and chromium in rocks [951].

Site Assessment-Related Information Provided by Shineldecker (Potential Site-Specific Contaminants that May be Associated with a Property Based on Current or Historical Use of the Property) [490]:

Raw Materials, Intermediate Products, Final Products, and Waste Products Generated During Manufacture and Use:

- Cobalt

Other Associated Materials:

- Fluorides

Metabolism/Metabolites [940]:

The ability of a number of metals and organic chemicals to induce metallothionein synthesis in primary rat hepatocytes cultures was tested to determine whether metallothionein induction in vivo results from a direct effect on the liver or an indirect, physiologic response to the agent. Hepatocytes were exposed to metals (zinc, cadmium, mercury, manganese, lead, cobalt, nickel, and vanadium) or organic compounds (ethanol, urethane, L-2-oxothiozolidine 4-carboxylate, or dexamethasone) and were assayed for metallothionein by the cadmium/hemoglobin radioasay. Cell viability was monitored by protein synthesis activity and cellular potassium ion concentration. Increases in metallothionein concentrations were noted for zinc (22 fold), mercury (6.4 fold), cadmium (4.8 fold), cobalt (2.4 fold), nickel (2.2 fold), and dexamethasone (4.5 fold). However, maximum tolerated concentrations of manganese, lead, vanadium, ethanol, urethane, and L-2-oxothiozolidine did not increase metallothionein. Zinc, cadmium, mercury, cobalt, nickel and dexamethasone induce metallothionein in vitro and are direct inducers of metallothionein

synthesis in hepatic tissue. [Bracken WM, Klaassen CD; J Toxicol Environ Health 22 (2): 163-74 (1987)].

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

W.Low (Water Concentrations Considered Low):

No information found.

W.High (Water Concentrations Considered High):

No information found.

W.Typical (Water Concentrations Considered Typical):

Typical Ocean Concentrations:

EPA 1981: 0.0054 mg/l [83].

Typical Freshwater Concentrations:

EPA 1981: 0.00008 mg/l [83].

Median Concentration for North American Rivers: 10 ug/L [190].

Large Public Water Supplies: < 2.7 ug/L [190].

Estimated median for river water: 0.3 ug/L [190].

California, 1986: Ambient background level for water was 1 ug/l [222].

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

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

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

Although most of the lab tests done to develop water quality criteria and other benchmarks were originally based on "total" values rather than "dissolved" values, some regulatory authorities nevertheless recommend comparing criteria with dissolved or acid soluble metals concentrations. EPA has given many reasons

why water quality criteria should be compared to acid soluble values (USEPA; Ambient Water Quality Criteria Document : Nickel, 1985 update) [35]. For detailed discussion, see the Laboratory and/or Field Analyses section (far below).

EPA 1996 IRIS database information on nickel soluble salts in general (various CAS numbers) and several other nickel compounds [893]:

Ambient Water Quality Criteria for Aquatic Organisms:

Acute Freshwater: 1.4E+3 ug/L [893].

Note: the above criteria is the same one published several years earlier for nickel in general, CAS 7440-02-0) (values in ug/L [446];

Freshwater Acute Criterion: 1,400 Hardness dependent criterion rounded to two integers (100 mg/L CaCO3 used). Note from Roy Irwin: This was evidently rounded to nearest two significant digits to arrive at the value of 1,400; the actual calculated value is 1418, based on the equation: acute = e (0.8460 [ln(hardness)] +3.3612) where "e" = exponential [649]. Further clarification:

e is the base of natural logarithms and numerically equals 2.72 (rounded), and In(hardness) equals the natural logarithm of the measured hardness (Gary Rosenlieb, National Park Service, Personal Communication, 1997).

Chronic Freshwater: 1.6E+2 ug/L [893].

Note: the above criteria is the same one published several years earlier for nickel in general, CAS 7440-02-0) (values in ug/L [446];

Freshwater Chronic Criteria: 160 Hardness dependent criteria (100 mg/L CaCO3 used).

Note from Roy Irwin: This was evidently rounded to the nearest two significant digits to arrive at the value of 160, the actual calculated value is 158, based on the equation: chronic = e(0.8460 [ln(hardness)] +1.1645) where "e" = exponential [649]. Further clarification:

e is the base of natural logarithms and numerically equals 2.72 (rounded), and In(hardness) equals the natural logarithm of the measured hardness (Gary Rosenlieb, National Park Service, Personal Communication, 1997).

Marine Acute: 7.5E+1 ug/L [893].

Older reference for nickel in general, CAS 7440-02-0) (values in ug/L [446]:

Marine Acute Criteria: 75

Marine Chronic: 8.3E+0 ug/L [893].

Older reference for nickel in general, CAS 7440-02-0) (values in ug/L [446]: Marine Chronic Criteria: 8.3.

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

Discussion: Criteria were derived from a minimum data base consisting of acute and chronic tests on a variety of species. The freshwater criteria are hardness dependent. Values given here are calculated at a hardness of 100 mg/L CaCO3. A complete discussion can be found in the referenced notice [893].

Criteria Federal Register Notice Number: 51 FR 4366 [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].

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 Nickel, CAS # 7440-02-0 (ug/L):

NATIONAL AMBIENT WATER QUALITY CRITERION - ACUTE: 1400

NOTE: The above is a hardness dependent criterion (100 mg/L CaCO3 was used to calculate the above concentration). For sites with different water hardness, site-specific criteria should be calculated with the following formula:

Acute = e(0.8460[ln(hardness)] +3.3612) where "e" = exponential [649]. Note: Same as IRIS 1996 EPA equation given above [893]. Further clarification:

e is the base of natural logarithms and numerically equals 2.72 (rounded), and In(hardness) equals the natural logarithm of the measured hardness (Gary Rosenlieb, National Park Service, Personal Communication, 1997).

NATIONAL AMBIENT WATER QUALITY CRITERION - CHRONIC: 160

The above is a hardness dependent criterion (100 mg/L CaCO3 was used to calculate the above concentration). For sites with different water hardness, site-

specific criteria should be calculated with the following formula:

Chronic = e(0.8460 [ln(hardness)]+1.1645) where "e" = exponential [649]. Note: Same as IRIS 1996 EPA equation given above [893]. Further clarification:

e is the base of natural logarithms and numerically equals 2.72 (rounded), and In(hardness) equals the natural logarithm of the measured hardness (Gary Rosenlieb, National Park Service, Personal Communication, 1997).

SECONDARY ACUTE VALUE: No information found.

SECONDARY CHRONIC VALUE: No information found.

LOWEST CHRONIC VALUE - FISH: < 35

LOWEST CHRONIC VALUE - DAPHNIDS: < 5

LOWEST CHRONIC VALUE - NON-DAPHNID INVERTEBRATES: 128.4

LOWEST CHRONIC VALUE - AQUATIC PLANTS: 5

LOWEST TEST EC20 - FISH: 62

LOWEST TEST EC20 - DAPHNIDS: 45

SENSITIVE SPECIES TEST EC20: 11

POPULATION EC2O: 215

Other Misc. General Concern Levels for Water Concentrations:

A State of California recommendation based on direct toxicity was that 2.6 ug/L be the water quality criteria (6.7 ug/l was an adverse effects level) [222].

Colorado specified a hardness dependent

equation as the acute general aquatic life water quality standard for nickel in 1991; at a hardness of 100 mg/L, the standard is 922.2 ug/L [659].

NOTE: The above is a hardness-dependent criteria (100 mg/L CaCO3 was used to calculate the above concentration). For sites with different water hardness, site-specific criteria should be calculated with the following formula:

Acute = 0.5 e(0.76[ln(hardness)] +4.02) where "e" = exponential [659].

Colorado specified a separate hardness dependent equation as the chronic water quality standard for general aquatic life for nickel 1991; at a hardness of 100 mg/L, the standard is 96 ug/L [659].

NOTE: The above is a hardness-dependent criteria (100 mg/L CaCO3 was used to calculate the above concentration). For sites with different water hardness, site-specific criteria should be calculated with the following formula:

Chronic = e(0.76[ln(hardness)]-1.06) where "e" = exponential [659].

W.Plants (Water Concentrations vs. Plants):

LC50 for Chlorella algae 0.5 mg/L [970].

Colorado specified an agricultural water quality standard of 200 ug/L nickel in 1991 [659].

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 7440-02-0, NICKEL, the benchmark is 0.2 mg/L (groundwater or porewater).

W.Invertebrates (Water Concentrations vs. Invertebrates):

LC50 Daphnia magna 0.85 mg/L [970].

LC50s for Acartia clausi and Acartia tonsa (both Calanoid copepod) were 2.076 mg/L (ppm) for a 96-hr exposure, and 0.460 mg/L for a 72-hr exposure, respectively [998].

LC50s for Amnicola sp. (Spire snail) ranged from 11.4 to 21.2 mg/L for 96-hr exposures [998].

LC50s for Chironomus sp. (midge) were 10.2 and 8.6 mg/L for 24- and 96-hr exposures, respectively [998].

LC50s for Crangon crangon (common shrimp) ranged from 100 to 330 mg/L for 48-hr exposures [998].

LC50s for Daphnia pulicaria (water flea) ranged from 0.697 to 3.757 mg/L (ppm) for 48-hr exposures, with most values above 1.800 mg/L [998].

LC50s for Trichoptera (Caddisfly order) were 48.4 and 30.2 mg/L for 24- and 96-hr exposures, respectively [998].

W.Fish (Water Concentrations vs. Fish):

LC50s for various fish 0.05 (trout) to 5.27 (bluegill) mg/L [970].

LC50s for Cyprinus carpio (common, mirror, colored, carp) were 38.3, 28.9 and 10.4 mg/L (ppm) for 24-, 48- and 96-hr exposures, respectively [998].

LC50s for Fundulus diaphanus (banded killifish) were 63.1, 50.0 and 46.1 mg/L (ppm) for 24-, 48- and 96-hr exposures, respectively [998].

LC50s for Morone saxatilis (striped bass) were 10.0, 8.5 and 6.3 mg/L (ppm) for 24-, 48- and 96-hr exposures, respectively [998].

LC50 for Mystus vittatus (catfish) was 255 mg/L (ppm) for a 96-hr exposure [998].

LC50s for Pimephales promelas (fathead minnow) ranged from 2.916 to 17.678 mg/L (ppm) for 96-hr exposures, with most values below 9.100 mg/L [998].

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]:

CAS 7440-02-0, NICKEL (AS NICKEL SULFATE HEXAHYDRATE)

SPECIES	WATER CONCENTRATION (ppm)
Rat (test species)	0.00000
Short-tailed Shrew	514.12500
Little Brown Bat	888.61300
White-footed Mouse	332.26300
Meadow Vole	581.51900
Cottontail Rabbit	275.54900
Mink	285.73700
Red Fox	203.92600
Whitetail Deer	114.09900

In order to evaluate recondite toxicity of nickel (Ni), rats of both sexes were exposed to 5 ppm Ni in drinking water for life. The 104 rats were given Ni, and a control group containing 104 rats each received the following essential metals in water (ppm): zinc 50, manganese 10, copper 5, chromium 5, cobalt 1, molybdenum 1. There was some increased growth in the Ni-fed rats, but the metal was virtually innocuous, not affecting the survival, longevity, incidence of tumors, or specific lesions. ... The feeding of Ni was associated with increased concentrations of chromium in heart and spleen, and manganese in the kidney, and decreased copper in the lung and spleen, zinc in lung, and manganese in spleen. Ni did not accumulate in tissues. ... [Schroeder HA et al; J Nutrit 104: 239 (1974)] [940].

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

EPA 1995 Region 9 Tap Water Preliminary Remediation Goal: 7.3E+02 nickel soluble salts ug/L (CAS 7440-02-0) [868].

EPA 1996 IRIS database information on nickel soluble salts in general (various CAS numbers) and for several other nickel compounds [893]:

Maximum Contaminant Level Goal (Value is listed for both nickel soluble salts, nickel subsulfide, and nickel carbonyl):

Value: 0.1 mg/L nickel [893].

Since this value is listed in "nickel" units and applies to several nickel species, it can evidently be taken as the benchmark for nickel in general.

Reference: 55 FR 30370 (07/25/90)

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

Discussion: EPA is proposing to regulate nickel based on its potential adverse effects (reduced body and liver weights) reported in a 2-year dietary study in rats. The MCLG is based upon a DWEL of 0.58 mg/L and an assumed drinking water contribution of 20 percent [893]..

Maximum Contaminant Level (MCL) [893]:

Value: 0.1 mg/L nickel (Value is listed for nickel soluble salts, nickel subsulfide, and nickel carbonyl):

Since this value is listed in "nickel" units and applies to several nickel species, it can evidently be taken as the benchmark for nickel in general.

Same EPA benchmark for nickel (100 ug/l) previously listed as a Federal Drinking Water Standard (USEPA/Office of Water; Federal-State Toxicology and Risk Analysis

Committee. Summary of State and Federal Drinking Water Standards and Guidelines, 11/93) [940]. Same level also listed as EPA health based limit in 1996 [952].

Reference: 55 FR 30370 (07/25/90)

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

Discussion: EPA is proposing an MCL equal to the proposed MCLG of 0.1 mg/L.

Ambient Water Quality Criteria for Human Health [893].

Water & Fish: 1.34E+1 ug/liter

Fish Only: 1.0E+2 ug/liter

Reference: 51 FR 43665 (12/03/86)

Contact: Criteria and Standards Division / OWRS / (202)260-1315

Discussion: The WQC of 1.34E+1 ug/L is based on consumption of contaminated aquatic organisms and water. A WQC of 1.0E+2 ug/L has also been established based on consumption of contaminated aquatic organisms alone.

Note: the above criteria are the same ones published several years earlier for nickel in general, CAS 7440-02-0) (values in ug/L [446]:

Human Health for Carcinogens (risk of one additional case in 1 million, 1E-06):

Published Criteria for Water and Organisms: 13.4

Published Criteria for Organisms Only: 100

IRIS Recalculated (9/90) Criteria for Water and Organisms: 510

IRIS Recalculated (9/90)

Criteria for Organisms Only: 3,800

EPA 1996 Health Advisory for nickel while MCL is remanded: 1E-01 mg/L [952].

EPA 1996 IRIS database information on nickel soluble salts in general (various CAS numbers) [893]:

> Crit. Dose: 5 mg/kg-day [Study 1 NOAEL(adj)] UF: 300 MF: 1
>
> RfD for nickel soluble salts: 2E-2 mg/kg-day Confidence: Medium [893]. RfD for Nickel in general (CAS number 7440-02-0): not listed in 1996 IRIS [893]. However, RfD for nickel in general, CAS 7440-02-0 given as 2E-02 mg/kg/day in another 1996 EPA document [952].
>
> 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].

State Drinking Water Guidelines [940]:

> (AZ) ARIZONA 150 ug/l [USEPA/Office of Water; Federal-State Toxicology and Risk Analysis Committee (FSTRAC). Summary of State and Federal Drinking Water Standards and Guidelines (11/93)].
>
> (ME) MAINE 150 ug/l [USEPA/Office of Water; Federal-State Toxicology and Risk Analysis Committee (FSTRAC). Summary of State and Federal Drinking Water Standards and Guidelines (11/93)].
>
> (MN) MINNESOTA 100 ug/l [USEPA/Office of Water; Federal-State Toxicology and Risk Analysis Committee (FSTRAC). Summary of State and Federal Drinking Water Standards and Guidelines (11/93)].

Bureau of Land Management RMC Benchmarks, 1995: Risk Management Criteria (RMC) developed for the mostly dry BLM lands in the western U.S. These risk management criteria should be used by the land manager as a cautionary signal that potential health hazards are present and that natural resource management or remedial actions are

indicated [715]. Exceedances of the criteria should be interpreted as follows [715]:

Less than criteria: low risk
1-10 times the criteria: moderate risk
10-100 times the criteria: high risk
>100 times the criteria: extremely high risk

Human RMC criteria for nickel in surface waters. These categories of humans not exposed to surface waters with concentrations of nickel exceeding the below RMCs are not expected to experience adverse toxic effects [715]:

Camp host: 6194 ug/L
Child Camper: 5688 ug/L
Boater: 22121 ug/L
Swimmer: 9578 ug/L

Human RMC criteria for nickel in ground water. These categories of humans not exposed to ground waters with concentrations of nickel exceeding the below RMCs are not expected to experience adverse toxic effects [715]:

Child resident (living on properties adjacent to BLM lands): 9 ug/L

Camp host: 74 ug/L
Child Camper: 203 ug/L
Worker: 155 ug/L
Surveyor: 1548 ug/L

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

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

Water bodies are often marked by heterogeneity of the distribution of undissolved materials [691]. The size of

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

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

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

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

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

as when ferric oxide coats or covers benthic organisms. Another factor to consider: contaminants carried downstream by erosion of bottom sediments or colloids can be mobilized when they come in contact with different physical/chemical environments downstream (for example, a tributary bringing low pH into the system).

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

> There is no question that dissolved metals are critical to fish and invertebrates, but less well recognized is the potential impact and movement of metals in colloids. The possibility of having colloidal material present means there is a readily available supply of metals in a state in which the metals can quickly be reduced and mobilized. In river banks, reducing environments form just under the surface quickly. Toxic metals of concern would include zinc, lead, copper, and cadmium.
>
> Colloids do move in surface water (for example, transport of metal in colloids 140 miles downstream of Leadville, CO), but also in groundwater, especially related to radionuclides.
>
> Colloidal metals may effect biota more than is widely recognized. Brown trout are effected by colloids which travel kind of like dissolved fractions, don't settle out. There may be little understood colloidal pathways of metals to fish, for example. Colloidal metals become part of the caddis cast which are ingested, once part of acid gut, metals can be released. On the Arkansas River of Colorado below Leadville, the dissolved metals have gone down with treatment, but Will Clements of CSU has discovered the toxicity has not been reduced to the same extent as have the dissolved metals. Treatment has not eliminated colloidal fractions loaded with cadmium and copper, and this is possibly impacting the fish.
>
> In rivers, there is annual flushing of the colloids, loads are much greater during runoff.

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

Sed.Low (Sediment Concentrations Considered Low):

No information found.

Sed.High (Sediment Concentrations Considered High):

NOAA National Status and Trends Program (1984-1990) [698]: "High" concentration for nickel in fine-grained sediment (n=233) = 69 ug/g dry weight at 4.6% TOC dry weight. The above concentration was adjusted for sediment grain-size in the following way: the raw concentrations were divided by the fraction of particles less than or equal to 64 um. "High" NOAA concentrations are equal to the geometric mean plus one standard deviation on the log normal distribution [696].

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

Analyses of sewage sludges from 50 publicly owned treatment works by the U.S. Environmental Protection Agency (1985): The mean concentration for nickel was 133.9 ppm (dry weight) [347].

Analyses of 74 Missouri sludges (1985): The median for nickel was 33.5 ppm (dry weight), the range for nickel was 10-13,000 ppm (dry weight) [347].

Freshwater Sediment Concentrations Considered Elevated:

Texas: The statewide 90th percentile value was 31.8 mg/kg dry weight [7].

Great Lakes Harbors, EPA 1977: Sediments having concentrations higher than 50 mg/kg dry weight were classified as "heavily polluted [145]."

Sed.Typical (Sediment Concentrations Considered Typical):

NOAA National Status and Trends Program (1984-1990) [698]: Geometric mean for nickel in fine-grained sediment (n=233) = 34 ug/g dry weight at 1.4% TOC dry weight. The above concentration was adjusted for sediment grain-size in the following way: the raw concentrations were divided by the fraction of particles less than or equal to 64 um.

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

Averages and ranges of concentrations of elements in soils and other surficial materials in the United States (1971): The mean for nickel was 20 ppm, the range was <5-700 ppm [347].

Freshwater Sediment Concentrations (Dry Weight) not Considered Elevated:

Great Lakes Harbors, EPA 1977: Sediments having sediment concentrations lower than 20.0 mg/kg were classified as "non polluted [145]."

International Joint Commission, 1988: The International Joint Commission considered <32.8 mg/kg as a background sediment level [145]. The control site in one Great Lakes study had a sediment concentration of 21.2 mg/kg [145].

Concentrations from Buffalo National Wildlife Refuge, Texas [401]: Sediment concentrations of nickel ranged from 5.8 mg/kg dry weight at site SW to 15.0 mg/kg dry weight at site SPI. These concentrations are below known concern levels or levels considered to be elevated [7,140,143,145, 233, 366, 416]. Soil concentrations from site DLB (11-12 mg/kg dry weight were not highly elevated compared to other published values [83,366].

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):

Various Concern Levels for Sediment Concentrations (Dry Weight):

EPA Region 6, 1973: The concentration proposed by EPA Region 6 as a guideline for determining acceptability of dredged sediment disposal was 50 mg/kg [143].

Ontario, 1978: The concentration proposed by the Ontario Ministry of the Environment as a threshold for evaluations of dredging projects was 25.0 mg/kg [145]. Ontario 1993, lowest effect level 16 mg/kg dry wt [761]. Ontario 1993, severe effect level 75 mg/kg dry wt [761].

International Joint Commission, 1988: The IJC suggested sediment concentrations not exceed background levels of 32.8 mg/kg [145].

AET values from EPA 1988: The apparent effects threshold concentrations for nickel in sediments proposed for Puget Sound ranged from 140 mg/kg dry weight (Benthic Species) to 140 mg/kg dry weight (amphipods) [416]. Although the authors of the Puget Sound AETs have cautioned that Puget Sound AETs may not be appropriate for comparison with data from other geographic areas, so few concern levels for this chemical have been published that the proposed Puget Sound concern level is included in this text as an item of interest.

NOAA 1995 Concern Levels for Coastal and Estuarine Environments: After studying its own data from the National Status and Trends Program as well as many literature references concerning different approaches to determining sediment criteria, NOAA suggested that the potential for biological effects of this contaminant sorbed to sediments was highest in sediments where its concentration exceeded the 51.6 ppm dry weight Effects Range-Median (ERM) concentration and was lowest in sediments where its concentration was less than the 20.9 ppm dry weight Effects Range-Low (ERL) concentration [664]. To improve the original 1990 guidelines [233], the 1995 report included percent (ratios) incidence of effects for ranges below, above, and between the ERL and ERM values. These numbers represent the number of data entries within each concentration range in which biological effects were observed divided by the total number of entries within each range [664] :

<ERL	1.9
ERL-ERM	16.7
>ERM	16.9

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks (to be considered of

little risk, field measured or estimated concentrations should be below all of the following concentrations)[652]:

For nickel, CAS #7440-02-0:

EFFECTS RANGE - LOW (NOAA): 21 mg/kg dry wt.

EFFECTS RANGE - MEDIAN (NOAA): 52 mg/kg dry wt.

Guidelines for the pollutional classification of Great Lakes harbor sediments (1977): Less than 20 ppm of nickel indicates nonpolluted sediment. Between 20 and 50 ppm of nickel indicates moderately polluted sediment. Greater than 50 ppm of nickel indicates heavily polluted sediment [347,761].

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

St. Lawrence River Interim Freshwater Sediment Criteria, 1992. No effect level: 35 mg/kg dry weight. Minimal effect level: 35 mg/kg dry weight. Toxic effect level: 61 mg/kg dry weight [761].

Environment Canada Interim Sediment Quality Assessment Values, 1994. Threshold effect level: 18 mg/kg dry weight. Probable effect level: 35.9 mg/kg dry weight [761].

New York 1994 Freshwater Dredging Sediment Criteria. No values given [761].

Sed.Plants (Sediment Concentrations vs. Plants):

No information found.

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

No information found.

Sed.Fish (Sediment Concentrations vs. Fish):

No information found.

Sed.Wildlife (Sediment Concentrations vs. Wildlife or

Domestic Animals):

No information found.

Sed.Human (Sediment Concentrations vs. Human):

Bureau of Land Management RMC Benchmarks, 1995: Risk Management Criteria (RMC) developed for the mostly dry BLM lands in the western U.S. These risk management criteria should be used by the land manager as a cautionary signal that potential health hazards are present and that natural resource management or remedial actions are indicated [715]. Exceedances of the criteria should be interpreted as follows [715]:

Less than criteria: low risk
1-10 times the criteria: moderate risk
10-100 times the criteria: high risk
>100 times the criteria: extremely high risk

Human RMC criteria for nickel in sediments. These categories of humans not exposed to sediments with concentrations of nickel exceeding the below RMCs are not expected to experience adverse toxic effects [715]:

Camp host: 3094 mg/kg
Child Camper: 1422 mg/kg
Boater: 11061 mg/kg
Swimmer: 4789 mg/kg

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

No information found.

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

Soil.Low (Soil Concentrations Considered Low):

No information found.

Soil.High (Soil Concentrations Considered High):

Aerial fallout from a nickel smelter at Port Colborne, Ontario, Canada, resulted in accumulation of nickel ranging from 600 to 6455 mg/kg in the organic soil of a farm. /Nickel and cmpd/ [USEPA; Health Assessment Document: Nickel p.29 (1983) EPA 600/8-83-012] [940].

Analyses of sewage sludges from 50 publicly owned

treatment works by the U.S. Environmental Protection Agency (1985): The mean concentration for nickel was 133.9 ppm (dry weight) [347].

Analyses of 74 Missouri sludges (1985): The median for nickel was 33.5 ppm (dry weight), the range for nickel was 10-13,000 ppm (dry weight) [347].

Soil.Typical (Soil Concentrations Considered Typical):

EPA 1981: 40 mg/kg dry weight is typical [83].

Typical Igneous Rocks (Earth's Crust) Concentrations: EPA 1981: 75 mg/kg dry weight [83].

Averages and ranges of concentrations of elements in soils and other surficial materials in the United States (1971): The mean for nickel was 20 ppm, the range was <5-700 ppm [347].

Average concentration of nickel in the earth's crust is 60-90 mg/kg. (Nat'l Research Council Canada; Effects of Nickel in the Canadian Environ p.27 (1981) NRCC No.18568) [366].

The Earth's crust contains 0.018% nickel, although the core is believed to be much richer [271].

Uncontaminated agricultural soils in Canada generally contain less than 30 mg nickel (Ni)/kg. Soils derived from serpentine rock may contain up to 25,000 mg Ni/kg, although a more typical value is 1000 mg/kg. Accumulations of Ni in soil exceeding 1000 mg/kg occur within 1-2 km of large nickel smelters. /Nickel and cmpd/ (Nat Research Council Canada; Effects of Nickel in the Canadian Envir p.28, 1981, NRCC No. 18568) [940].

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

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

Soil criteria for evaluating the severity of contamination under the Dutch Soil Cleanup (Interim) Act (1982): 50 ppm indicates a background concentration of nickel. 100 ppm indicates a moderate soil contamination of nickel. 500 ppm indicates a threshold value of nickel which

requires immediate cleanup [347].

Soil cleanup criteria for decommissioning industrial sites in Ontario (1987): For agricultural land nickel should not exceed 32 ppm, for residential or parklands nickel should not exceed 200 ppm, and for commercial or industrial parklands nickel should not exceed 200 ppm [347]. Proposal of Ontario Ministry of Agriculture and Food for MAC in soils treated with sewage sludge: 32 ppm dry weight (published in Tokyo; work done for Ontario) [719].

Suggested cleanup guidelines for inorganic contaminants in acidic soils in Alberta (1987): Acceptable level of nickel for acidic soils is 250 ppm [347].

Maximum allowable concentration of nickel in soil in the Soviet Union is 4.0 ppm (1984) [347].

Other Maximum Allowable Concentration (MAC) levels of nickel (ppm dry weight): 50 (Stuttgart), 20 (London-value given for soluble pool of the element), 35 (London-value given for soluble pool of the element) [719].

Proposal of European Economic Commission for MAC in soils treated with sewage sludge: 30 (50) ppm dry weight (London). The value in parentheses is for mandatory concentrations [719].

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

In 1981 the U.S. Environmental Protection Agency proposed 200 ppm as an upper limit for nickel for sewage sludges suitable for land application [391].

Maximum cumulative addition of metals (kg/ha) from sewage sludge to Maryland agricultural soil (1986): For a soil with a cation exchange capacity (CEC) of less than 5 meq/100 g addition of nickel should not exceed 140 kg/ha, for a soil with a CEC greater than 5 addition of nickel should not exceed 280 kg/ha [347].

Maximum cumulative addition of metals (kg/ha) from sewage sludge to Massachusetts agricultural soil (1983): For a soil with a cation exchange capacity of less than 5 meq/100 g nickel should not be added at greater than 56 kg/ha, for a soil with a CEC greater than 5 meq/100 g nickel should not be added

at greater than 112 kg/ha [347].

Maximum cumulative addition of metals from sewage sludge that may be added to Minnesota soils used for growing food crops (1987): For a soil with a cation exchange capacity (CEC) of less than 5 meq/100 g nickel should not be added at greater than 56 kg/ha, for a soil with a CEC between 5 and 15 meq/100 g nickel should not be added at greater than 112 kg/ha, for a soil with a CEC greater than 15 nickel should not be added at greater than 224 kg/ha [347].

Maximum cumulative addition of metals (kg/ha) from sewage sludge recommended for privately owned Missouri farmland (1988): For a soil with a cation exchange capacity (CEC) of less than 5 meq/100 g nickel should not be added at greater than 140 kg/ha, for a soil with a CEC between 5 and 15 nickel should not be added at greater than 280 kg/ha, for a soil with a CEC greater than 5 meq/100 g nickel should not be added at greater than 560 kg/ha [347].

Cumulative amounts of metals per hectare that may be added to New York State soils with sewage sludge (1988): For productive agricultural soil nickel should not be added at greater than 34 kg/ha, for less productive agricultural soil nickel should not be added at greater than 50 kg/ha, and for forests nickel should not be added at greater than 168 kg/ha [347].

Maximum heavy metal loading (kg/ha) recommended for sludge applications to privately owned Oregon farmland (1984): For soils with a cation exchange capacity (CEC) of less than 5 meq/100 g nickel should not be added at greater than 50 kg/ha, for soil with a CEC between 5 and 15 nickel should not be added at greater than 100 kg/ha, and for a soil with a CEC greater than 15 meq/100 g nickel should not be added at greater than 200 kg/ha [347].

Maximum cumulative additions of metals from sewage sludge that may be added to Vermont soils, by soil texture (1984): For loamy sand nickel should not be added at greater than 56 kg/ha, for fine sandy loam nickel should not be added at greater than 112 kg/ha, and for a clay loam nickel should not be added at greater than 224 kg/ha [347].

Maximum cumulative applications of nickel from sewage sludge that may be added to Wisconsin soils (1985): For a soil with a cation exchange capacity

(CEC) of less than 5 meq/100 g nickel should not be added above 50 kg/ha, for a soil with a CEC between 5 and 10 nickel should not be added above 100 kg/ha, for a soil with a CEC between 11 and 15 meq/100 g nickel should not be added at greater than 150 kg/ha, for a soil with a CEC greater than 15 nickel should not be added at greater than 200 kg/ha [347].

Soil limit values determined by the Council of European Communities for the addition of heavy metals from sewage sludge to soil with a pH of 6.0-7.0 (1986): The limit value for nickel is 30-75 ppm [347].

Soil.Plants (Soil Concentrations vs. Plants):

Levels of nickel (ppm dry weight) considered phytotoxic: 100 (Vienna), 100 (Warsaw), 100 (Tokyo), 100 (Warsaw) and 100 (Ontario) [719].

Acceptable level of nickel for production of healthy food: 35 ppm dry weight (Moscow) [719].

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

> For CAS 007440-02-0 (NICKEL), the benchmark is 30 mg/kg in soil (WILL and SUTER, 1994)

Low Ni concentrations (2.5-20 ppm) stimulated the growth of some soil fungi (eg Spicaria violacea, Aspergillus ornatus, Penicillium chrysogenum, and Penicillium canescens). The lowest tolerance to Ni was observed with Rhizopus arrhizus, the highest tolerance with Trychoderma polysporum. Most of the fungi were inhibited by Ni at all concentrations (2.5-100 ppm: P canescens, P rubrum, Penicillium strain no 38, R arrhizus, and T polysporum). Ni accumulation in the fungi was highest in R arrhizus and lowest in T polysporum. Thus, the soil fungi can be used as indicators of soil pollution by heavy metals. The fungi with relatively high resistance to the metals can be used for the reclamation of heavily polluted soils. [Zabawski J; Bioindyk Skazen Przem Roln Mater Pokonf p.303-15 (1983)] [940].

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]:

For Nickel, CAS 7440-02-0:

SSL = 1600 mg/kg for ingestion pathway, non-cancer risk [952].

SSL = 13000 mg/kg for inhalation pathway [952].

SSL = 7 to 130 mg/kg for protection from migration to groundwater at 1 to 20 Dilution-Attenuation Factor (DAF) [952].

EPA 1995 Region 9 Preliminary remediation goals (PRGs) for nickel soluble salts, CAS 7440-02-0, 1995 [868]:

Residential Soil: 1500 mg/kg wet wt. Nickel Soluble Salts

Industrial Soil: 34000 mg/kg wet wt. Nickel Soluble Salts

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 land uses are slightly lower concentrations than EPA Region III RBCs, which consider fewer aspects [903].

California modified Preliminary remediation goals

(PRGs) for nickel soluble salts, 1995 [868]:

Residential Soil: 150 mg/kg wet wt. Nickel Soluble Salts

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

21 mg/Kg dry weight [903].

Acceptable level of nickel for production of healthy food: 35 ppm dry weight (Moscow) [719].

Bureau of Land Management RMC Benchmarks, 1995: Risk Management Criteria (RMC) developed for the mostly dry BLM lands in the western U.S. These risk management criteria should be used by the land manager as a cautionary signal that potential health hazards are present and that natural resource management or remedial actions are indicated [715]. Exceedances of the criteria should be interpreted as follows [715]:

Less than criteria: low risk
1-10 times the criteria: moderate risk
10-100 times the criteria: high risk
>100 times the criteria: extremely high risk

Human RMC criteria for nickel in soil. These categories of humans not exposed to soil with concentrations of nickel exceeding the below RMCs are not expected to experience adverse toxic effects [715]:

Child resident (living on properties adjacent to BLM lands): 40 mg/kg
Camp host: 1032 mg/kg
Child Camper: 711 mg/kg
ATV Driver: 14517 mg/kg
Worker: 1548 mg/kg
Surveyor: 15485 mg/kg

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

No information found.

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

Tis.Plants:

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

No information found.

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

Typical plant concentration: 3 ppm dry weight; high concentrations in plants (over 300 ppm) found only in nickel enriched areas; toxicity to plants: severe [951].

Possibly useful; reference: Turnquist, T.D.; Urig, B.M.; Hardy, J.K. 1990. Nickel Uptake by the Water Hyacinth. J Environ Sci Health A-Sci E 25(8): 897-912. TD Turnquist/Mt Union Coll/Dept Chem/Alliance, OH 44601.

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:

At Buffalo Lake National Wildlife Refuge, Texas, the highest concentration of nickel in any biota was 1.5 mg/kg dry weight (0.372 mg/kg wet weight) in a whole body sample of crayfish [401].

Clams are generally better accumulators of nickel than fish [83,95]. Eleven of 77 Trinity River samples were above 0.9 mg/kg, including samples of Asian clam flesh and crayfish. The clam and crayfish samples were from site 5 downstream of Fort Worth, and the other samples exceeding 0.9 mg/kg were from sites downstream of Dallas [201].

The following information summarizes data gathered from the NOAA National Status and Trends (NS&T) Program for the year 1990 [697]:

For nickel in mussels and oysters combined (n=214), the Geometric Mean was 1.7 ug/g dry and the "high" concentration was 3.3 ug/g dry weight [697]. NOAA "high" concentrations are equal to the geometric mean plus one standard deviation on the log normal distribution [696].

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):

Bureau of Land Management RMC Benchmarks, 1995: Risk Management Criteria (RMC) developed for the mostly dry BLM lands in the western U.S. These risk management criteria should be used by the land manager as a cautionary signal that potential health hazards are present and that natural resource management or remedial actions are indicated [715]. Exceedances of the criteria should be interpreted as follows [715]:

Less than criteria: low risk
1-10 times the criteria: moderate risk
10-100 times the criteria: high risk
>100 times the criteria: extremely high risk

Human RMC criteria for nickel in fish consumed by humans. These categories of humans not exposed to fish with concentrations of nickel exceeding the below RMCs are not expected to experience adverse toxic effects [715]:

Child resident (living on properties adjacent to BLM lands): 1567 ug/kg
Camp host: 3226 ug/kg
Child Camper: 8888 ug/kg

EPA 1995 Region 3 Risk based concentration (RBC) table states that nickel in general, although not considered a carcinogen, should not exceed 27 mg/kg [903].

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:

Fish concentrations above 0.9 mg/kg wet weight nickel appear to be elevated values in relationship to relatively unpolluted sites in the Southwest studied by the Fish and Wildlife Service [65,201]. None of the wet weight values in this study at Buffalo Lake National Wildlife Refuge, Texas, exceeded this level or seemed high in comparison with other studies [401].

The following text is quoted from the Trinity River Report [201] for reference comparison with values from other areas): Nickel concentrations above the detection limit (0.02 mg/kg) were found in 60 of 77 Trinity River samples. Maximum Level: The highest nickel concentration, 12 mg/kg, was from a composite sample of mosquitofish from site 25, a storm drain in downtown Fort Worth where a spill of nickel had occurred a year before our collections. This is a very high nickel concentration; the highest nickel concentration recorded in a survey of Pennsylvania fish from 14 sites was 0.41 mg/kg [57]. Concentrations above 0.9 mg/kg nickel appear to be elevated values in relationship to relatively unpolluted sites in the Southwest studied by our agency. Eleven of 77 Trinity River samples were above 0.9 mg/kg, including samples of Asian clam flesh, crayfish, mosquitofish, freshwater drum, longnose gar, and Mississippi map turtles. The clam and crayfish samples were from site 5 downstream of Fort Worth, and the other samples exceeding 0.9 mg/kg were from sites downstream of Dallas. Clams are generally better accumulators of nickel than fish [83,95].

Gradient Monitoring Levels [201]: Nickel showed a tendency to increase from upstream to downstream in mosquitofish. Sediment concentrations of nickel from our sites 9 through 12 exceeded statewide 90th percentiles in at least 50% of the historical records from 1974 to 1985 [7].

In a recent study in a rural area of Texas, we found concentrations of 0.05 to 0.21 mg/kg nickel in mosquitofish from the Rio Grande River at Big Bend National Park [65]. These concentrations were lower than all but 5 of 24 mosquitofish from the Trinity River [201].

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]:

CAS 7440-02-0 NICKEL (AS NICKEL SULFATE HEXAHYDRATE)

SPECIES	NOAEL (mg/kg/day)	FOOD CONCEN-TRATION (ppm)
Rat (test species)	40.0000	0.0000
Short-tailed Shrew	113.1080	188.5130
Little Brown Bat	142.1780	426.5340
White-footed Mouse	99.6790	644.9800
Meadow Vole	79.2980	697.8220
Cottontail Rabbit	26.6360	134.8680
Mink	28.2880	206.4820
Red Fox	17.2200	172.2040
Whitetail Deer	7.4720	242.6250

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

Baseline data on Ni accumulation in organs and tissues, and their variations with age, sex, and habitat in Japanese serows (Capricornus crispus) were determined. The animals were killed during the winter 1981-82 in the Gifu and Nagano Prefectures, Japan. The Ni concentrations were measured by flame absorption spectrometry. On a wet wt basis, the mean Ni concentration in muscle, liver, kidneys, and the whole body of fetuses (gestation age 0.3-0.7 yr, N= 13) was 0.01, 0.02, 0.01, and 0.03 ug/g, respectively; in fawns (age 0.0-0.5 yr, N= 12) was 0.02, 0.03, 0.04, was 0.05 ug/g, respectively; yearlings (age 0.5-2.5 yr, N= 6) was 0.01, 0.04, 0.04, and 0.07 ug/g, respectively; in adults (age

2.5 to 10 yr, N= 42) was 0.02, 0.05, 0.05, and 0.09 ug/g, respectively; and in adults (age 10 to 17.5 yr, N= 17) was 0.02, 0.06, 0.05, and 0.11 ug/g, respectively. The bile Ni content ranged from 0.05 to 0.08 ug/ml. High concentrations were found in the gastrointestinal organs. The mean Ni concentration in fleece of fawns, yearlings, and adults (age 2.5 to 10 yr) was 0.29, 0.25, and 0.16 ug/g, respectively. Bone samples of two adult serows contained 0.25 to 0.54 ug/g. The body burden of fetuses was low (<1%) compared with those of their mothers. There was no significant difference in Ni concentration between collection location. The body burden of Ni agreed well with the concentration found in food plants. /Nickel salts/ [Honda K et al; Arch Environ Contam Toxicol 16: 551-61 (1987)] [940].

Tissue Concentration Results from Buffalo Lake National Wildlife Refuge, Texas [401]:

> The concentrations of nickel ranged from 0.23 mg/kg dry weight (0.073 wet weight) in a yellow mud turtle sample from site SPI to 1.5 mg/kg dry weight (0.372 mg/kg wet weight) in a whole body sample of crayfish from site SR.

Other Tissue Concentrations from Texas: Eleven of 77 Trinity River samples were above 0.9 mg/kg, including samples of Asian clam flesh, crayfish, mosquitofish, freshwater drum, longnose gar, and Mississippi map turtles [201].

Ingestion of nickel had a relatively low degree of toxicity. Dogs are able to tolerate doses of metallic nickel as high as 3 g/kg body wt. (International Labour Office. Encyclopedia of Occupational Health and Safety. Volumes I and II. New York: McGraw-Hill Book Co., 1971. 932) [940].

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

No information found.

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

See also Tis.Fish, A) above.

FDA Requirements [940]:

Substance added directly to human food affirmed as generally recognized as safe (GRAS). [21 CFR 184.1537 (4/1/88)].

EPA 1995 Region 3 Risk based concentration (RBC) table states that nickel in general, although not considered a carcinogen, should not exceed 27 mg/kg [903].

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

EPA 1996 IRIS database information on nickel soluble salts in general (various CAS numbers) [893]:

Crit. Dose: 5 mg/kg-day [Study 1 NOAEL(adj)] UF: 300 MF: 1

RfD: 2E-2 mg/kg-day [893,868]. Confidence: Medium [893].

Tis.Misc. (Other Tissue Information):

No information found.

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

Plants take up nickel from soil, groundwater, sewage sludge, fertilizers, and air pollution [83]. Animals take up nickel from industrial sources, contaminated air, contaminated water, and contaminated food [83].

Nickel BCFs (bioconcentration factors) range from 40-100 in fish and 100-259 in invertebrates [959]. Preliminary data suggests the potential for bioaccumulation or bioconcentration of nickel is moderate for the following biota: mammals, birds, and fish. It appears to be high to very high for mollusks, crustacea, lower animals, mosses, lichens, algae, and higher plants [83].

The best potential mediums for biological monitoring (including gradient monitoring) appear to include higher plants, mosses, and lichens [83]. Irwin found mosquitofish to be acceptable for gradient monitoring of nickel [201]. See also: Turnquist, T.D.; Urig, B.M.; Hardy, J.K. 1990. Nickel Uptake by the Water Hyacinth. J Environ Sci Health A-Sci E 25(8): 897-912. TD Turnquist/Mt Union Coll/Dept Chem/Alliance, OH 44601.

Biological Half-Life [940]:

On the basis of nickel values in air, plasma and urine in four nickel platers during one working week ... /the investigators/, assuming a one-compartment model, computed the biological half-life for nickel in plasma to

range from 20 to 34 hr and in urine from 17 to 39 hr. [Friberg, L., Nordberg, G.F., Kessler, E. and Vouk, V.B. (eds). Handbook of the Toxicology of Metals. 2nd ed. Vols I, II.: Amsterdam: Elsevier Science Publishers B.V., 1986.,p. V2 469].

Interactions:

Information from HSDB [940]:

The effect of nickel (Ni) on cadmium nephrotoxicity and hepatotoxicity in rats was investigated. The administration of Ni (6 mg/kg, ip, for 3 days) or cadmium (6 mg/kg, im, once) significantly enhanced the urinary excretion of alkaline phosphatase, lactate dehydrogenase, glutamate oxaloacetate transaminase, amino acids and proteins. In addition, it increased the activity of serum alkaline phosphatase, glutamate oxaloacetate transaminase, and glutamate pyruvate transaminase. These biochemical alterations in urine and serum were used as a measure of kidney and liver damage. Cadmium induced enzymuria, proteinuria, aminoaciduria and increased activity of serum enzymes were significantly less marked in animals pretreated with Ni than in controls. The accumulation of cadmium in kidneys and liver and its urinary excretion were unaffected by Ni pretreatment. [Tandon SK et al; Ann Clin Lab Sci 14 (5): 390-6 (1984)].

Estuarine/marine fungi tolerated nickel (Ni) better when grown on a nutrient medium supplemented with seawater, than when exposed on a non-marine medium. The ameliorating effect of seawater or salinity on the toxicity of nickel to mycelial proliferation was related to the magnesium, rather than to the sodium or chlorine ions in the marine systems. This interaction between magnesium and Ni was not unique to marine fungi, as magnesium also decreased the toxicity of Ni to non-marine fungi. [Babich H, Stotzky G; Water Air Soil Pollut 19 (2): 193-202 (1983)].

An interaction of nickel with copper and zinc is suspected since anemia-induced nickel deficiency is only partially corrected with nickel supplementation in rats receiving low dietary copper and zinc. [Doull, J., C.D.Klassen, and M.D. Amdur (eds.). Casarett and Doull's Toxicology. 3rd ed., New York: Macmillan Co., Inc., 1986. 610].

The biocompatibility of a nickel chromium molybdenum dental casting alloy and an in vitro explant culture of gingival cells was determined. Results indicate that cultured gingival cells have a well preserved ultrastructure and synthesized fibronectin (the main

glycoprotein involved in adhesion to substrates). Type III collagen production decreased significantly in the cultures exposed to the dental alloy. [Exbrayant P et al; Biomaterials 8 (5): 385-92 (1987)].

Exposure of Nostoc muscorum to different concentrations of nickel and silver caused reduced growth, carbon fixation, heterocyst production, and nitrogenase activity and increase potassium ion and sodium ion loss. Ascorbic acid and glutathione were more protective against silver than nickel insult. Metal induced inhibition of growth and carbon fixation was equally ameliorated by methionine. The level of protection afforded by cysteine was 27% for nickel and 22% for silver. [Rai LC, Raizada M; Ecotoxicol Environ Safety 14 (1): 12-21 (1987)].

The effects of carcinogenic nickel compounds on natural killer cell function were studied in rats. The protective effects of manganese were also investigated. Male WAG rats were injected intramuscularly with 20 mg metallic nickel powder, 5 mg nickel subsulfide, 20 mg nickel oxide, and 0 or 20 mg mananese with or without rat fibroblast interferon. Rats given nickel subsulfide had a tumor incidence of 2%, whereas 46.7% of the rats given nickel powder developed tumors. All tumors developed at the injection site. More than 70% of the tumor bearing rats died with lung or lymph node metastases within 3 months after the primary tumors were detected. Interferon had little effect on tumor incidence or time to tumor development. Nickel oxide did not induce any tumors. Manganese protected against tumor induction. Only 20% of rats given nickel powder plus manganese developed tumors. Rats that developed tumors showed persistent decreases in natural killer cell activity. The lower the natural killer cell activity, the earlier the tumors developed. Manganese almost completely prevented the decrease in PBMC natural killer cell activity when given along with powdered nickel. [Judde JG et al; JNCI 78 (6): 1185-90 (1987)].

Uses/Sources:

Although nickel occurs naturally in rivers from soil erosion, it is usually elevated at least four times above background levels in most urban settings, with asbestos being one potential source [35]. Other sources include air pollution deposition from burning of fossil fuels, operation of motor vehicles, smelters, electroplating facilities, scrap yards, and various industrial sources [35]. Meteorites sometimes contain up to 20% nickel [271]. Pure nickel is used in electron tubes and in the galvanic (plating) industry, where many objects must be coated with nickel before they can be chrome plated [271]. Nickel is also a common contaminant in sludges generated by sewage treatment plants [94]. Nickel is also

present in the leachate of some municipal landfills [80]. Stainless steel, an alloy of iron and chromium, may contain up to 35% nickel [271]. Special nickel alloys include alnico, cunife, and cunico, used as permanent magnets, and nichrome, which is used as electrical heating elements in many household appliances [271].

Plants take up nickel from soil, groundwater, sewage sludge, fertilizers, and air pollution [83]. Animals take up nickel from industrial sources, contaminated air, contaminated water, and contaminated food [83].

Major Uses [940]:

Nickel plating; for various alloys such as new silver, chinese silver, german silver; for coins, electrotypes, lightning rod tips, electrical contacts & electrodes, spark plugs, machinery parts; catalyst for hydrogenation of org substances; in mfr of monel metal, stainless steels, & nickel chrome resistance wire; in alloys for electronic & space applications [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 932].

Intermediate in synthesis of acrylic esters [International Labour Office. Encyclopedia of Occupational Health and Safety. Vols. I&II. Geneva, Switzerland: International Labour Office, 1983. 1438].

It is extensively used for making stainless steel & other corrosion resistant alloys ... Tubing made of copper nickel alloy ... Used in making desalination plants ... In making nickel steel armor plate & burglar proof vaults ... Nickel added to glass gives green color. [Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. B-26].

Component of ferrous alloys [SRI].

Component of nonferrous alloys [SRI].

Component of permanent magnets [SRI].

Nickel is/ used as a catalyst ... Used in the hydrogenation of fats and oils ... . [21 CFR 184.1537 (4/1/86)].

Component of ceramics [SRI].

Component of batteries & fuel cells [SRI].

Chem int for nickel compounds [SRI].

In surgical & dental prostheses [International Labour Office. Encyclopedia of Occupational Health and Safety. Vols. I&II. Geneva, Switzerland: International Labour Office, 1983. 1438].

As antistatic coating [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 3(78) 169].

Use in cooling towers as anodic inhibitor [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 21(83) 73].

Natural Sources [940]:

Abundance in earth's crust 0.018%. ... Occurs free in meteorites. Found in many ores as sulfides, arsenides, antimonides & oxides or silicates; chief sources incl chalcopyrite ... Pyrrhotite, pentlandite ((FE,NI)958) & garnierite (3(MG,NI)O.-2SIO2.2H2O); other ores incl niccolite ... & Millerite (NIS). [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 932].

Nickel constitutes 0.03% Of the particulate matter suspended in atmosphere. In addition, there is evidence that pure nickel powders ... Of less than 1 u in size are deposited as meteoritic dust from stratosphere. /NICKEL AND NICKEL CMPD/ [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. V2 131 (1973)].

Natural sources of airborne particles that contain nickel include soil, sea, volcanoes, forest fires, and vegetation. /Nickel and nickel cmpd/ [Davies CN; Atmos Envir 8: 1069-79 (1974) as cited in Nat'l Research Council Canada; Effects of Nickel in the Canadian Environ p.60 (1981) NRCC No.18568].

Average concn of nickel in the earth's crust is 60-90 mg/kg. /Nickel and nickel cmpd/ [Nat'l Research Council Canada; Effects of Nickel in the Canadian Environ p.27 (1981) NRCC No.18568].

Artificial Sources [940]:

Environmenal accumulation: nickel powder's incr usage enhances probability of its appearance in atmosphere @ nickel prodn plants. The avg concn in usa in 1964 & 1965 was 340 ng/cu m. Nickel finds its way into atmosphere as result of combustion of coal, diesel oil & fuel oil. [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. V2 131 (1973)].

Food processing methods apparently add to the nickel levels already present in foodstuffs via (1) leaching from nickel containing alloys in food processing equipment made from stainless steel, (2) the milling of flour, and (3) catalytic hydrogenation of fats and oils by use of nickel catalysts. [USEPA; Ambient Water Quality Criteria Document : Nickel p.C-7 (1980) EPA 400/5-80-060].

Forms/Preparations/Formulations:

Finely divided nickel is used as a catalyst in many reactions, such as the hydrogenation of organic compounds [271]. It is a good catalyst for reactions with carbon monoxide because of the formation of such compounds as nickel carbonyl, a rare example of a compound in which a metal has a zero valence [271].

Radionuclides:

The symbol for Nickel-63 is 63Ni, the atomic number is 28, the half-life is 100 years, and beta emission is the major form of decay [674].

The symbol for Nickel-65 is 65Ni, the atomic number is 28, the half-life is 2.5 hours, and beta emission is the major form of decay [674].

Information from HSDB [940]:

Grades: electrolytic; ingot; pellets; shot; sponge; powder; high purity strip; single crystals (wire 2X0.05-0.005 IN) [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 819].

Ferronickel has a nickel content of 24-48%. Also available are electrolytic cathode sheets and pellets produced by the decomposition of nickel carbonyl. [CONSIDINE. CHEMICAL AND PROCESS TECHNOL ENCYC 1974 p.766].

Pellets (99.99%), spherical powder, spray powder, nickel flour; high density grade for electronics; nickel flour for shielding coatings, HP pellets for vacuum and chemical work, spherical powder for spray work [Kuney, J.H. and J.N. Nullican (eds.) Chemcyclopedia. Washington, DC: American Chemical Society, 1988. 197].

6-12 mm; 3 mm; -20, +45 mesh; -100, +200 mesh, -200, +325 mesh; -325 mesh; about 2 microns, 99.9% purity grades [Kuney, J.H. and J.N. Nullican (eds.) Chemcyclopedia. Washington, DC: American Chemical Society, 1988. 197].

99% to 99.99%, solid to submicron powders [Kuney, J.H. and J.N. Nullican (eds.) Chemcyclopedia. Washington, DC: American Chemical Society, 1988. 197].

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

Solubilities [940]:

Insol (sic, actually "relatively insoluble") in water, ammonia; sol in dil nitric acid; slightly sol in hydrochloric acid, sulfuric acid [Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. B-110].

Vapor Pressure [940]:

1 MM HG @ 1810 DEG C [Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. D-194].

Molecular Weight [940]:

58.70 [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 932].

Density/Specific Gravity [940]:

8.90 [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 932].

Boiling Point [940]:

2730 deg C [Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. B-110].

Melting Point [940]:

1455 deg C [Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. B-110].

Odor [940]:

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

Color/Form [940]:

SILVERY METAL [Weast, R.C. (ed.) Handbook of Chemistry

and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. B-110].

Other Chemical/Physical Properties [940]:

Heat capacity @ 25 deg c: 6.23 Cal/g-atom/deg c; mohs' hardness 3.8; Latent heat of fusion 73 cal/g; electrical resistivity @ 20 deg c: 6.844 Microohms/cm; burns in oxygen, forming nickel oxide; decomp steam @ a red heat; slowly attacked by dil hydrochloric or sulfuric acid; readily attacked by nitric acid; five naturally occurring isotopes: 58 (67.76%); 60 (26.16%); 61 (1.25%); 62 (3.66%); 64 (1.16%); ARTIFICIAL ISOTOPES: 56; 57; 59; 63; 65-67 [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 932].

Not attacked by fused alkali hydroxides [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 932].

Readily fabricated by hot & cold working; takes high polish; excellent resistance to corrosion [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 818].

Atomic number 28; valence 2; seldom 1,3,4 [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 932].

Dark gray powder or crystal; Pyrophoric [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 818].

Crystallizes as metallic cubes [Sax, N.I. Dangerous Properties of Industrial Materials. 6th ed. New York, NY: Van Nostrand Reinhold, 1984. 1990].

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

Environmental Fate [940]:

The atmosphere is a major conduit for nickel as particulate matter. Contributions to atmospheric loading come from both natural sources and anthropogenic activity, with input from both stationary and mobile sources. Various dry and wet precipitation processes remove particulate matter as wash out or fallout from the atmosphere with transfer to soils and waters. Soil borne nickel may enter waters by surface runoff or by percolation into ground water. Once nickel is in surface and ground water systems, physical and chemical

interactions (complexation, precipitation/dissolution, adsorption/desorption, and oxidation/reduction) occur that will determine its fate and that of its constituents. /Nickel and cmpd/ [USEPA; Health Assessment Document: Nickel p.20 (1983) EPA 600/8-83-012].

Biodegradation [940]:

No data was found to suggest that nickel is involved in any biological transformation in the aquatic environment. [Callahan, M.A., M.W. Slimak, N.W. Gabel, et al. Water-Related Environmental Fate of 129 Priority Pollutants. Volume I. EPA-440/4 79-029a. Washington, DC: U.S.Environmental Protection Agency, December 1979.,p. 15-6].

Absorption, Distribution and Excretion [940]:

Approx 50% of inhaled nickel dust is deposited on bronchial mucosa & swept upward in mucus to be swallowed, about 25% is exhaled, & rest is deposited in the pulmonary parenchyma. ... IV injected nickel salts disappear quickly from blood, indicating widespread distribution in tissues. In spite of firmly chelated nickel in human tissues, retention of newly acquired nickel in tissues is transient & poor. ... Under certain pathological conditions ... Incr amt of nickel are found in blood ... Excretion of ingested nickel cmpd is mainly fecal, with only about 10% in urine; this ... Is noted ... In dogs & humans. Excretion of absorbed nickel & iv admin nickel cmpd is primarily urinary (about 60%) & rest fecal, presumably from bile, which indicates an enterohepatic transfer. /NICKEL CMPD/ [Venugopal, B. and T.D. Luckey. Metal Toxicity in Mammals, 2. New York: Plenum Press, 1978. 291].

Use of urinary & plasma concentrations of nickel as indicators of exposure to nickel is discussed. [TOLA S ET AL; ANN CLIN LAB SCI 8 (6): 498 (1978)].

Diurnal variations in nickel concentrations in plasma & urine were studied. [HOGETVEIT AC ET AL; ANN CLIN LAB SCI 8 (6): 497 (1978)].

Thirty-five lung pairs obtained during autopsy from randomly selected patients were investigated by particle induced x-ray emission for overall & regional elemental content determination. Nickel distribution seems to be related to air pollution peculiar to /BELGIUM/. [BARTSCH P ET AL; ARCH ENVIRON HEATLH 37 (2): 111-7 (1982)].

Therapeutic or normal level of nickel in human blood was determined: 0.011 mg%, 0.11 ug/ml. [Winek, C.L. Drug and Chemical Blood-Level Data 1985. Pittsburgh, PA: Allied

Fischer Scientific, 1985.].

Retained esp by lung, 38% of its uptake being present after 72 hr, while the brain, with 16.7%, Also retained larger amt than other tissues. [Browning, E. Toxicity of Industrial Metals. 2nd ed. New York: Appleton-Century-Crofts, 1969. 252].

Pancreatic juice from 19 subjects (11 males, age 20-68 yr) and 8 females, age 45-64 yr) were analyzed for cadmium, lead, copper, iron, manganese, cobalt, chromium, nickel, zinc, magnesium, and calcium and protein. Diagnoses were: normal, 5; early pancreatic cancer, 9; and chronic pancreatitis, 5. None had symptoms suggestive of disturbances in endocrine and exocrine functions of the pancreas. Concentrations of metals and protein in pancreatic juice were similar for males and females and did not change with pathological alterations of the pancreas. Assuming the flow rate of pancreatic juice to be 1500-2000 ml/day, the daily excretions of metals into duodenum via pancreatic juice were calculated as follows (umoles of metal/day): cadmium, 0.012-0.012; lead, 0.216-0.288; copper, 6.20-8.26; iron, 2.34-3.12; manganese, 0.100-0.133; cobalt, 0.165-0.220; zinc, 7.46-9.94; chromium, 0.084-0.112; magnesium, 274.1-365.4; nickel, 1.64-2.18; and calcium, 0.221-0.295. Toxic (cadmium and lead) and essential metals (copper, zinc, iron, manganese, chromium, and nickel) were excreted daily. [Ishihara N et al; Arch Environ Health 42 (6): 356-60 (1987)].

A study of nickel and chromium concentrations in human pulmonary tissue was conducted. Tissue samples obtained at autopsy from the lung of 15 deceased persons were analyzed for nickel and chromium. Information on occupation and smoking habits was obtained from family members. None of the subjects had any occupational exposure to nickel or chromium, and all subjects lived in rural areas in West Germany, with no established metal industries. Substantial variations in nickel and chromium concentration occurred within single lung and between individuals. Chromium concentrations ranged from 29.0 to 324.2 ng/g, median 204 ng/g. Nickel concentrations ranged from 16.3 to 60.2 ng/g, median 25.6 ng/g. Intrapulmonary variations in chromium and nickel content had coefficients of variation of 26 to 104 percent and 31 to 159 percent, respectively. The concentrations of nickel and chromium in the upper lung were 1.3 to 1.9 times higher than in other areas. Average concentrations of both metals were highest in the hilar tissue, averaging 3 to 5 times that of pulmonary tissue. Chromium concentrations averaged 1.3 to 3.0 times higher in smokers than in nonsmokers. Nickel concentrations showed no correlation with smoking habits. [Raithel HJ et al; Am

Ind Med 12 (1): 55-70 (1987)].

After acute or chronic exposure of rats ... By inhalation, incr in nickel occur predominantly in microsomal & supernatant fractions of lung & liver. After chronic exposure, incr amt of ni are also observed in nuclear & mitochondrial fraction of the lung. /NICKEL AND NICKEL CMPD/ [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. V11 100 (1976)].

Significant uptake & accum occurred in 20, 40, & 80 mg nickel/l in 96 hr expt. Mussels secreted byssal threads in concn of 20 mg nickel/l, but not in higher concn. [FRIEDRICH AR ET AL; BULL ENVIRON CONTAM TOXICOL 16 (6): 750 (1976)].

Absorption of nickel is small from ordinary diets. Excretion is primarily through feces; however significant amt can be lost in sweat. /NICKEL/ [Osol, A. and J.E. Hoover, et al. (eds.). Remington's Pharmaceutical Sciences. 15th ed. Easton, Pennsylvania: Mack Publishing Co., 1975. 969].

Nickel is present in lung, liver, kidney, & intestine of most stillborn infants. Concn in lung incr with age. In rats bones accumulate a major portion of incr intake. ... Nickel has been found in bile. /NICKEL/ [Casarett, L.J., and J. Doull. Toxicology: The Basic Science of Poisons. New York: MacMillan Publishing Co., 1975. 488].

Baseline data on Ni accumulation in organs and tissues, and their variations with age, sex, and habitat in Japanese serows (Capricornus crispus) were determined. The animals were killed during the winter 1981-82 in the Gifu and Nagano Prefectures, Japan. The Ni concentrations were measured by flame absorption spectrometry. On a wet wt basis, the mean Ni concentration in muscle, liver, kidneys, and the whole body of fetuses (gestation age 0.3-0.7 yr, N= 13) was 0.01, 0.02, 0.01, and 0.03 ug/g, respectively; in fawns (age 0.0-0.5 yr, N= 12) was 0.02, 0.03, 0.04, was 0.05 ug/g, respectively; yearlings (age 0.5-2.5 yr, N= 6) was 0.01, 0.04, 0.04, and 0.07 ug/g, respectively; in adults (age 2.5 to 10 yr, N= 42) was 0.02, 0.05, 0.05, and 0.09 ug/g, respectively; and in adults (age 10 to 17.5 yr, N= 17) was 0.02, 0.06, 0.05, and 0.11 ug/g, respectively. The bile Ni content ranged from 0.05 to 0.08 ug/ml. High concentrations were found in the gastrointestinal organs. The mean Ni concentration in fleece of fawns, yearlings, and adults (age 2.5 to 10 yr) was 0.29, 0.25, and 0.16 ug/g, respectively. Bone samples of two adult serows contained 0.25 to 0.54 ug/g.

The body burden of fetuses was low (<1%) compared with those of their mothers. There was no significant difference in Ni concentration between collection location. The body burden of Ni agreed well with the concentration found in food plants. /Nickel salts/ [Honda K et al; Arch Environ Contam Toxicol 16: 551-61 (1987)].

Laboratory and/or Field Analyses:

Many methods have been used to monitor for nickel [861,1001,1003,1004,1005,1006]. EPA methods recommended depend on the application: whether for drinking water [40 CFR Part 141 and 1005,1006,1008], NPDES discharge permits [40 CFR 136 and 1005,1006], CERCLA [861,1005,1006], RCRA [861,1005,1006], or low-detection-limit water-quality based permitting [1001,1003,1004]. Other agencies (USGS, APHA, ASTM, NOAA, etc. also publish different "standard methods." If one simply wants to know whether or not the concentration exceeds EPA criteria or various low concentration benchmarks for humans, fish, or wildlife, it is not always too clear which "standard method" is optimum, although some might argue that for water, the 1996 EPA methods 1640 and 1669 (see details below) should apply.

Any low concentration criteria or benchmarks may require relatively rigorous methods, while routine applications may require only the older standard inductively- coupled plasma (ICP) analyses. ICP/MS detection limits for water can be as low as 0.0005 mg/L (40 CFR Part 141.23, part of the Drinking Water Regulations).

However, detection limits should be no higher than comparison benchmarks or criteria for various media (water, sediments, soil, tissues, etc), some of which are somewhat low (see sections above). Otherwise, the detection limits should usually not exceed the following default concentrations often recommended by the Fish and Wildlife Service and the National Park Service (Roy Irwin, National Park Service, Personal Communication, 1997):

Tissue detection limits 0.50 ppm dry weight

Sediment and Soil Detection Limits: 5 ppm

Water Detection Limits: If necessary for comparison with low criteria (EPA Water Quality Criteria are as low as 7.1 ug/L) or in areas where background levels are quite low, a water detection limit as low as 0.029 ug/L is possible using EPA method 1640 [1001]. This element can also be analyzed by EPA method 1638, an ICP/MS method, to a detection limit of 0.33 ug/l or by method 1639 to a detection limit of 0.65 ug/L, but lower detection limits are available with EPA method 1640. Otherwise, a historical default water detection limit of 0.005 ppm (mg/L) is often acceptable (for example, in areas where higher concentrations are found as background levels). One publication stated that the median Concentration for North American Rivers was 10 ug/L [190].

Although most of the lab tests done to develop water quality criteria and other benchmarks were originally based on "total" values rather than "dissolved" values, the lab settings were typically fairly clean and the numbers generated by the lab tests are therefore often even more comparable to field "dissolved" values than to field "total" values (Glen Suter, Oak Ridge National Lab, Personal Communication, 1995). As of January 1995, the U.S. EPA was recommending that states use dissolved measurements in water quality standards for metals, in concert with recommendations EPA previously made for the Great Lakes [672].

The conversion factors recommended by EPA for converting total recoverable metals criteria to dissolved metal criteria were given as follows [672]:

Nickel conversion for acute criteria: 0.998; nickel conversion for chronic criteria: 0.997 (for example, total recoverable chronic nickel criteria x 0.997 = dissolved chronic nickel criteria). These same conversion factors were recommended by EPA for converting total recoverable lead to dissolved concentrations in the January 1997 draft EPA Guidelines for 5 year 305(B) assessments.

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

Acceptable containers (after proper cleaning per EPA protocols) for Antimony, Arsenic, Cadmium, Copper, Lead, Nickel, Selenium, Silver, Thallium, and Zinc: 500-mL or 1-L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid [1003].

Filtration and Acidification of Water Samples:

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.

Note: In more recent (1996) guidance related to the more rigorous method 1669, EPA clarified (some would say confused or added data variability) the issue of when to acidify by stating:

"Preservation recommendations for

Antimony, Arsenic, Cadmium, Copper, Lead, Nickel, Selenium, Silver, Thallium, and Zinc: Add 5 mL of 10% HN03 to 1-L sample; preserve on-site or immediately upon laboratory receipt" [1003].

Note: the nitric acid (triple distilled or not?) and dilution water (contaminated or not?) and containers (proper type, cleaned correctly or not?) used are all potential sources of contamination (see more detailed note below related to data variation factors).

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.

It is important to understand that contaminants data from different labs, different states, and different agencies, collected by different people, are often not very comparable (see also, discussion in the disclaimer section at the top of this entry).

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.

Other Details on 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. 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].

Note: In a study at Yellowstone Park, Soda Butte Creek, filtering and then acidifying of water samples was done in two ways: The first way was in the field, per original standard EPA suggestions in 40 CFR. The second way was in the in the lab after 6 to 8 days. On two dates, lab filtered and acidified water was always higher in dissolved copper, a somewhat counter-intuitive result (Al, Fe, Mn, Zn, and Ni showed the opposite trend, tending to be higher in field filtered and acidified samples). On a third date 6 lab filtered and acidified samples were higher in copper and 3 field filtered and acidified samples were

higher (Del Nimmo, USGS, personal communication, 1997).

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]. New EPA Method 1638 specifies:

> "Store the preserved sample for a minimum of 48 h at 0–4°C to allow the acid to completely dissolve the metal(s) adsorbed on the container walls. The sample pH should be verified as <2 immediately before withdrawing an aliquot for processing or direct analysis. If, for some reason such as high alkalinity, the sample pH is verified to be >2, more acid must be added and the sample held for sixteen hours until verified to be pH <2" [1003].

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. For EPA method 1638, the word shake appears in the "Alternate total recoverable digestion procedure":

> "..Tightly recap the container and shake thoroughly" [1003].

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].

Highlights from EPA Lab Method 1640: Determination of trace elements in ambient waters by on-line chelation preconcentration and inductively coupled plasma-mass spectrometry:

This method is for the determination of dissolved elements in ambient waters at EPA water quality criteria (WQC) levels using on-line chelation preconcentration and inductively coupled plasma-mass spectrometry (ICP-MS) [1003]. It may also be used for determination of total recoverable element concentrations in these waters [1003]. This method was developed by integrating the analytical procedures contained in EPA Method 200.10 with the quality control (QC) and sample handling procedures necessary to avoid contamination and ensure the validity of analytical results during sampling and analysis for metals at EPA WQC levels [1003]. This method contains QC procedures that will assure that contamination will be detected when blanks accompanying samples are analyzed [1003]. This method is accompanied by Method 1669: Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels (the "Sampling Method") [1003]. The Sampling Method is necessary to ensure that contamination will not compromise trace metals determinations during the sampling process [1003].

This method is applicable to the following elements:

Cadmium (Cd), Copper (Cu), Lead (Pb), and Nickel (Ni) [1003].

Many of the requirements for this method are similar to those for other EPA 1600 series methods [1003].

As of March 1997, the EPA 1600 series methods had not yet been officially approved in 40 CFR for use in NPDES permits, but the improvements in these methods were suggested by EPA staff to be wise practice when attempting low detection limit analyses for metals [1003].

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

Acid solubilization is required before the determination of total recoverable elements to aid breakdown of complexes or colloids that might influence trace element recoveries [1003].

This method should be used by analysts experienced in the use of inductively coupled plasma mass spectrometry (ICP-MS), including the interpretation of spectral and matrix interferences and procedures for their correction; and should be used only by personnel thoroughly trained in the handling and analysis of samples for determination of metals at EPA WQC levels [1003]. A minimum of six months' experience with commercial instrumentation is recommended [1003].

Sample preservation—Preservation of samples and field blanks for both dissolved and total recoverable elements may be performed in the field when the samples are collected or in the laboratory [1003]. However, to avoid the hazards of strong acids in the field and transport restrictions, to minimize the potential for sample contamination, and to expedite field operations, the sampling team may prefer to ship the samples to the laboratory within 2 weeks of collection [1003]. Samples and field blanks should be preserved at the laboratory immediately when they are received [1003]. For all metals, preservation involves the addition of 10% HNO_3 to bring the sample to pH <2 [1003]. For samples received at neutral pH, approx 5 mL of 10% HNO_3 per liter will be required [1003].

Store the preserved sample for a minimum of 48 h at 0–4°C to allow the acid to completely dissolve the metal(s) adsorbed on the container walls [1003]. The sample pH should be verified as <2 immediately before an aliquot is withdrawn for processing or direct analysis [1003]. If, for some reason such as high alkalinity, the sample pH is verified to be >2, more acid must be added and the sample held for 16 h until verified to be pH <2 [1003].

Highlights from EPA Method 1669 for Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels [1003]:

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

This "field method details" protocol is for the collection and filtration of ambient water samples for subsequent determination of total and dissolved Antimony, Arsenic, Cadmium, Copper, Chromium III, Chromium VI, Lead, Mercury, Nickel, Selenium, Silver, Thallium, and

Zinc, at low (Water Quality Criteria Range) concentrations [1003]. It is designed to support the implementation of water quality monitoring and permitting programs administered under the Clean Water Act [1003].

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

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

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

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

There are numerous routes by which samples may become contaminated [1003]. Potential sources of trace metals contamination during sampling include metallic or metal-

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

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

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

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

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

An alternate grab sampler design is available [1003]. This grab sampler is used for discrete water samples and is constructed so that a capped clean bottle can be

submerged, the cap removed, sample collected, and bottle recapped at a selected depth [1003]. This device eliminates sample contact with conventional samplers (e.g., Niskin bottles), thereby reducing the risk of extraneous contamination [1003]. Because a fresh bottle is used for each sample, carryover from previous samples is eliminated [1003].

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

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

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

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

of ambient water samples) [1003].

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

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

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

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

Highlights from EPA Method 1639: Determination of trace elements in ambient waters by stabilized temperature graphite furnace atomic absorption:

This 1996 proposed EPA method provides procedures to

determine dissolved elements in ambient waters at EPA water quality criteria (WQC) levels using stabilized temperature graphite furnace atomic absorption (GFAA) [1003]. It may also be used to determine total recoverable element concentrations in these waters [1003].

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

This method was developed by integrating the analytical procedures contained in EPA Method 200.9 with the stringent quality control (QC) and sample handling procedures necessary to avoid contamination and ensure the validity of analytical results during sampling and analysis for metals at EPA WQC levels [1003]. This method contains QC procedures that will ensure that contamination will be detected when blanks accompanying samples are analyzed [1003]. This method is accompanied by Method 1669: Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels (the "Sampling Method") [1003]. The Sampling Method is necessary to ensure that contamination will not compromise trace metals determinations during the sampling process [1003].

Many of the requirements for this method are similar to those for other EPA 1600 series methods [1003].

This method may be used with the following metals [1003]:

Antimony (Sb), CAS 7440-36-0
Cadmium (Cd), CAS 7440-43-9
Trivalent Chromium, CAS 16065-83-1
Nickel (Ni), CAS 7440-02-0
Selenium (Se), CAS 7782-49-2
Zinc (Zn), CAS 7440-66-6

For dissolved metal determinations, samples must be filtered through a 0.45-um capsule filter at the field site [1003]. The filtering procedures are described in the Sampling Method [1003]. Except for trivalent chromium, the filtered samples may be preserved in the field or transported to the laboratory for preservation [1003]. Procedures for field preservation are detailed in the Sampling Method; procedures for laboratory preservation are provided in this method [1003]. To determine trivalent chromium, a field preparation step, which is described in the Sampling Method, is used to isolate the trivalent chromium [1003].

To determine total recoverable analytes in ambient water samples, a digestion/extraction is required before analysis when the elements are not in solution (e.g., aqueous samples that may contain particulate and suspended solids) [1003].

Construction materials—Only the following materials should come in contact with samples: fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, polypropylene, polysulfone, or ultrapure quartz [1003]. PTFE is less desirable than FEP because the sintered material in PTFE may contain contaminates and is susceptible to serious memory contamination [1003]. Fluoropolymer or glass containers should be used for samples that will be analyzed for mercury because mercury vapors can diffuse in or out of the other materials resulting either in contamination or low-biased results [1003]. All materials, regardless of construction, that will directly or indirectly contact the sample must be cleaned using EPA procedures and must be known to be clean and metal free before proceeding [1003].

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

Serialization—It is recommended that serial numbers be indelibly marked or etched on each piece of Apparatus so that contamination can be traced, and logbooks should be maintained to track the sample from the container through the labware to injection into the instrument [1003]. It may be useful to dedicate separate sets of labware to different sample types; e.g., receiving waters vs. effluents [1003]. However, the Apparatus used for processing blanks and standards must be mixed with the Apparatus used to process samples so that contamination of all labware can be detected [1003].

Do not dip pH paper or a pH meter into the sample; remove a small aliquot with a clean pipet and test the aliquot [1003]. When the nature of the sample is either unknown or known to be hazardous, acidification should be done in a fume hood [1003].

Store the preserved sample for a minimum of 48 h at 0–4°C to allow the acid to completely dissolve the metal(s)

adsorbed on the container walls [1003]. The sample should then verified to be pH < 2 just before withdrawing an aliquot for processing or direct analysis [1003]. If for some reason such as high alkalinity the sample pH is verified to be > 2, more acid must be added and the sample held for 16 h until verified to be pH < 2 [1003].

One of the requirements for the alternate total recoverable digestion procedure is to tightly recap the container and shake thoroughly [1003].

Highlights from EPA Method 1638: Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma — Mass Spectrometry:

This 1996 proposed EPA method is for the determination of dissolved elements in ambient waters at EPA water quality criteria (WQC) levels using inductively coupled plasma-mass spectrometry (ICP-MS) [1003]. It may also be used for determination of total recoverable element concentrations in these waters [1003]. This method was developed by integrating the analytical procedures in EPA Method 200.8 with the quality control (QC) and sample handling procedures necessary to avoid contamination and ensure the validity of analytical results during sampling and analysis for metals at EPA WQC levels [1003]. This method contains QC procedures that will assure that contamination will be detected when blanks accompanying samples are analyzed [1003]. This method is accompanied by Method 1669: Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels ("Sampling Method") [1003]. The Sampling Method is necessary to assure that trace metals determinations will not be compromised by contamination during the sampling process [1003].

This method may be used with the following metals:

Antimony (Sb), CAS 7440-36-0
Cadmium (Cd), CAS 7440-43-9
Copper (Cu), CAS 7440-50-8
Lead (Pb), CAS 7439-92-1
Nickel (Ni), CAS 7440-02-0
Selenium (Se), CAS 7782-49-2
Silver (Ag), CAS 7440-22-4
Thallium (Tl), CAS 7440-28-0
Zinc (Zn), CAS 7440-66-6

As of March 1997, the EPA 1600 series methods had not yet been officially approved in 40 CFR for use in NPDES permits, but the improvements in these methods were suggested by EPA staff to be wise practice when attempting low detection limit analyses for metals [1003].

This method is not intended for determination of metals at concentrations normally found in treated and untreated discharges from industrial facilities [1003]. Existing regulations (40 CFR Parts 400–500) typically limit concentrations in industrial discharges to the mid to high part-per-billion (ppb) range, whereas ambient metals concentrations are normally in the low part-per-trillion (ppt) to low ppb range [1003].

The ease of contaminating ambient water samples with the metal(s) of interest and interfering substances cannot be overemphasized [1003]. This method includes suggestions for improvements in facilities and analytical techniques that should maximize the ability of the laboratory to make reliable trace metals determinations and minimize contamination [1003]. These suggestions are ...based on findings of researchers performing trace metals analyses [1003]. Additional suggestions for improvement of existing facilities may be found in EPA's Guidance for Establishing Trace Metals Clean Rooms in Existing Facilities, which is available from the National Center for Environmental Publications and Information (NCEPI) at the address listed in the introduction to this document [1003].

Clean and ultraclean—The terms "clean" and "ultraclean" have been applied to the techniques needed to reduce or eliminate contamination in trace metals determinations [1003]. These terms are not used in this method because of their lack of an exact definition [1003]. However, the information provided in this method is consistent with the summary guidance on clean and ultraclean techniques [1003].

The procedure given in this method for digestion of total recoverable metals is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L [1003]. For the analysis of samples containing higher concentrations of silver, succeedingly smaller volume, well-mixed sample aliquots must be prepared until the analysis solution contains <0.1 mg/L silver [1003].

Sample preservation—Preservation of samples and field blanks for both dissolved and total recoverable elements may be performed in the field at time of collection or in the laboratory [1003]. However, to avoid the hazards of strong acids in the field and transport restrictions, to minimize the potential for sample contamination, and to expedite field operations, the sampling team may prefer to ship the samples to the laboratory within two weeks of collection [1003]. Samples and field blanks should be preserved at the laboratory immediately upon receipt [1003]. For all metals, preservation involves the

addition of 10% HNO_3 to bring the sample to pH <2 [1003]. For samples received at neutral pH, approx 5 mL of 10% HNO_3 per liter will be required [1003].

Do not dip pH paper or a pH meter into the sample; remove a small aliquot with a clean pipet and test the aliquot [1003]. When the nature of the sample is either unknown or known to be hazardous, acidification should be done in a fume hood [1003].

Store the preserved sample for a minimum of 48 h at 0–4°C to allow the acid to completely dissolve the metal(s) adsorbed on the container walls [1003]. The sample pH should be verified as <2 immediately before withdrawing an aliquot for processing or direct analysis [1003]. If, for some reason such as high alkalinity, the sample pH is verified to be >2, more acid must be added and the sample held for sixteen hours until verified to be pH <2 [1003].

EPA 1996 IRIS database information on drinking water methods used for nickel soluble salts in general (various CAS numbers) [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 (EPA 249.2; SM 304); inductively-coupled plasma (EPA 200.7; SM 305); ICP mass spectrometry (EPA 200.8): PQL= 0.050 mg/L.