TOXICOLOGICAL ANALYSIS OF

OHIO BRINE CONSTITUENTS

AND THEIR POTENTIAL IMPACT ON

HUMAN HEALTH

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for
Governor's Oil and Gas
Review Commission
Columbus, Ohio

December, 1986

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TOXICOLOGICAL EVALUATION OF BRINE CONTAMINANTS

EXECUTIVE SUMMARY

Oil and gas drilling in the paleozoic formations in the state of Ohio
has been associated with the production of waste brines. Chemical
characterization of selected brine samples has only recently been
performed by the Underground Injection Control Section of the Division
of Oil and Gas at the Ohio Department of Natural Resources.
Preparatory to evaluating the potential impact of adverse brine
disposal on human resources such as drinking waters, is an evaluation
of the health-related standards for the individual chemical components
in brines.

This report represents a compilation of recent toxicological risk
assessment studies. Table 1 provides a list of published human health
and water quality standards for individual inorganic chemicals
identified in Ohio brines. Table 2 similarly provides a list of
published human health and water quality standards for individual
organic chemicals identified in Ohio brines and for several organic
chemical classes considered likely to be found in Ohio brines.

The full report has been divided into three sections:

SECTION 1.
Summary evaluation of water quality standards for inorganic elements
and compounds in Ohio brines.
    Available summarized data concerning individual elements, for which
standards have been promulgated, are appended. Data are derived from
the Wisconsin Department of Health and Social Services (1985), "Public
Health Related Groundwater Standards - Summary of Scientific Support
Documentation for NR 140.10."
    For each chemical, an abbreviated risk assessment summarizes the
following information:
    1. general chemical information;   8. teratogenicity/reproductive
    2. human exposure routes;   effects;
    3. acute toxicity;   9. environmental fate;
    4. chronic toxicity;   10. risk assessment;
    5. human health effects;   11. recommendations and
    6. mutagenicity;   conclusions;
    7. carcinogenicity;   12. references.

SECTION 2.
Summary evaluation of water quality standards for organic compounds in
Ohio brines (benzene, ethylbenzene, toluene, and xylenes).
    Available summarized data for these are appended. Data are derived
from the Wisconsin Department of Health and Social Services (1985 &
1986), and from the Harry G. Armstrong Aerospace Medical Research
Laboratory at Wright-Patterson Air Force Base, Ohio (1985), "The
Installation Restoration Program (IRP) Toxicology Guide."

Polynuclear aromatic hydrocarbons and phenolic compounds are major classes of organic chemicals which were examined in several Michigan brine samples, and they can be expected to occur in Ohio brines. Therefore, I have added the IRP summary environmental toxicology data for naphthalene and dimethylphenol, which contain generic information on standards for polynuclear aromatics and phenolic compounds respectively.

Again, for each organic chemical, an abbreviated risk assessment summarizes the information outlined above for inorganic chemicals. Additional comprehensive summary reports are appended for the organic contaminants measured or suspected in Ohio brines. Each report contains the following information:
1. Physicochemical Data;
2. Persistance in Soil-Water Systems;
3. Pathways of exposure;
4. Health Hazards Data;
5. Handling Precautions;
6. Emergency First Aid Treatment;
7. Environmental and Occupational Standards;
8. Chemical Usage;
9. Detailed Environmental Fate and Exposure Pathways;
10. Human Health Considerations; and,
11. Sampling and Analysis Considerations.

SECTION 3.
<u>Analysis of the Ohio brine contaminant data with suggestions for prioritization of chemicals with human health concerns.</u>

A primary goal of this report has been to compare analyses of chemical constituents in brine with existing regulatory status of these chemical parameters. From this exercise, a subset of brine chemicals which pose relatively greater environmental risks could be identified.

Two brine contaminant reports from the Ohio Department of Natural Resources (1986) and the Michigan Department of Natural Resources (1984) are evaluated and criticized. Average and maximum concentrations of selected contaminants are rated according to their suggested standards for potential risk in surface and groundwater contamination. Benzene, sodium and chloride are the contaminants which would require the highest amount of dilution with contaminant-free water to achieve drinking water quality.

Given the need to expand the sampling program for brine disposal problems, yet mindful of funding limitations for chemical analyses, I recommend that:
A. Inorganic analyses be prioritized to focus sodium (Na) and chloride (Cl). These chemicals represent by weight the most important brine contaminants. Analytical techniques for detecting and quantifying these parameters in the range of 10% of the secondary standards or health guidance levels would provide a powerful tool for estimating brine disposal impact upon drinking water supplies.

B. Organic analyses be prioritized to focus initially upon benzene. Measurable quantities of benzene were found in all Michigan Oilfield brines and other brine samples. Benzene was detected in all Ohio brine samples. Benzene poses high risks as a toxic substance, therefore drinking water quality recommendations are very restrictive.

C. Benzene analytical procedures in brine needs to be thoroughly examined and rigorously defined to insure that the sampling protocol is a high contaminant potential sample. Limits of benzene detection in various matrices need to be evaluated for brine samples and for dilution series.

D. The recommended water quality standards for polynuclear aromatic hydrocarbons and phenolic compounds warrents investigation of these compound classes for identification and quantification in brines. Analytical procedures similar to those devised for benzene analysis need to be developed. With answers to these analytical questions, polynuclear aromatic hydrocarbons and phenolic compounds may need to be added to benzene as standards monitoring parameters in brine disposal problems.

Table 1. Summary of Health and Water Quality Standards on Inorganic
Chemicals Identified in Ohio Brines.

Chemical	Standard	Source
Ag (Silver)	50 ug/l	WI (1985); U.S.EPA
As (Arsenic)	50 ug/l	WI (1985); U.S.EPA
B (Boron)	No Federal Standard	U.S.EPA (1986)
Ba (Barium)	1000 ug/l	WI (1985); U.S.EPA
Ca (Calcium)	No Federal Standard	U.S.EPA (1986)
Cd (Cadmium)	10 ug/l	WI (1985); U.S.EPA
Cl (Chlorine)	No Primary Standard Secondary Standard: 250,000 ug/l	U.S.EPA (1986)
Co (Cobalt)	No Federal Standard	U.S.EPA (1986)
CO (Carbonate)	No Federal Standard	U.S.EPA (1986)
Cr (Chromium)	50 ug/l	WI (1985); U.S.EPA
Cu (Copper)	No Federal Standard Proposed Maximum Contaminant Level Goal: 1,300 ug/l	U.S.EPA (1986)
Fe (Iron)	No Primary Standard Secondary Standard: 300 ug/l	U.S.EPA (1986)
HCO (Bicarbonate)	No Federal Standard	U.S.EPA (1986)
Hg (Mercury)	2 ug/l	WI (1985); U.S.EPA
I (Iodine)	No Federal Standard	U.S.EPA (1986)
K (Potassium)	No Federal Standard	U.S.EPA (1986)
Li (Lithium)	No Federal Standard	U.S.EPA (1986)

Standards reported as micrograms per liter (ug/l).

Sources: WI (1985); U.S.EPA: Standard established by the Wisconsin
Department of Health and Social Services and including an evaluation
of current and proposed U.S.EPA Drinking Water Standards either as
National Interim Primary Drinking Water Standards or as Maximum
Contaminant Levels.
        U.S.EPA (1986): evaluation of currently unregulated chemicals
as reported in personal communication with Ms. Jennifer Orme of the
U.S.EPA Office of Drinking Water October 31, 1986.

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Table 1. Continued.

Chemical	Standard	Source
Mg (Magnesium)	No Federal Standard	U.S.EPA (1986)
Mn (Manganese)	No Primary Standard Secondary Standard: 50 ug/l	U.S.EPA (1986)
Mo (Molybdenum)	No Federal Standard	U.S.EPA (1986)
Na (Sodium)	No Federal Standard Health Guidance Level: 20,000 ug/l	U.S.EPA (1986)
Ni (Nickel)	No Federal Standard Health Guidance Level: 150 ug/l	U.S.EPA (1986)
P (Phosphorous)	No Federal Standard	U.S.EPA (1986)
Pb (Lead)	50 ug/l	WI (1985); U.S.EPA
Se (Selenium)	10 ug/l	WI (1985); U.S.EPA
SO (Sulfate)	No Federal Standard Health Guidance Level: 400,000 ug/l	U.S.EPA (1986)
Sr (Strontium)	No Federal Standard	U.S.EPA (1986)
Ti (Titanium)	No Federal Standard	U.S.EPA (1986)
U (Uranium)	No Federal Standard Health Guidance Level: 10 pCi/l	WI (1985); U.S.EPA
V (Vanadium)	No Federal Standard	U.S.EPA (1986)
Zn (Zinc)	No Primary Standard Secondary Standard: 5000 ug/l	U.S.EPA (1986)

Standards reported as micrograms per liter (ug/l); Uranium reported as picocurie units of radioactivity per liter (pCi/l)

Sources: WI (1985); U.S.EPA: Standard established by the Wisconsin Department of Health and Social Services and including an evaluation of current and proposed U.S.EPA Drinking Water Standards either as National Interim Primary Drinking Water Standards or as Maximum Contaminant Levels.
U.S.EPA (1986): evaluation of currently unregulated chemicals as reported in personal communication with Ms. Jennifer Orme of the U.S.EPA Office of Drinking Water October 31, 1986.

Table 2. Summary of Health and Water Quality Standards on Selected Organic Chemicals.

a. Identified in Ohio Brines.

Chemical	Standard	Source
Benzene	0.67 ug/l	WI (1985); U.S.EPA
Ethylbenzene	1360 ug/l	WI (1986); U.S.EPA
Toluene	343 ug/l	WI (1985); U.S.EPA
Xylene	620 ug/l	WI (1985); U.S.EPA

b. Likely to Occur in Ohio Brine.

Chemical Class	Standard	Source
Polynuclear Aromatic Hydrocarbons	0.2 ug/l	EEC Directive (IRP Toxicology Guide)
Phenolic Compounds	0.5 ug/l	EEC Directive (IRP Toxicology Guide)

Standards reported as micrograms per liter (ug/l).

Sources: WI (1985); U.S.EPA: Standard established by the Wisconsin Department of Health and Social Services during 1985 and including an evaluation of current and proposed U.S.EPA Drinking Water Standards either as National Interim Primary Drinking Water Standards or as Maximum Contaminant Levels.

WI (1986); U.S.EPA: Similar Standards established by the Wisconsin Department of Health and Solcial Services during 1986.

EEC Directive (IRP Toxicology Guide): Standard established by the European Economic Community as maximum admissible concentrations relating to quality of water intended for human consumption. Reported in "The Installation Restoration Program Toxicology Guide." Vol. 1 (1985) prepared by Arthur D. Little, Inc. for the Harry G. Armstrong Medical Research Laboratory, Wright-Patterson AFB, OH 45433-6573.

SECTION 1: INORGANIC CHEMICAL STANDARDS AND EVALUATIONS

The inorganic parameters reviewed for water quality standards were selected from the list of inorganic chemicals reported in the appended table to "Preliminary Analyses of Ohio Oilfield Produced Brines for Selected Heavy Metals and Aromatic Hydrocarbons," (1986) by D.R. Christ and G. Hudak of the Ohio Department of Natural Resources, Division of Oil and Gas, Underground Injection Control Section. Table 1 summarizes the existing health and drinking water quality standards on these inorganic contaminants.

For eight parameters (Ag, As, Ba, Cd, Cr, Hg, Pb, and Se), health related primary drinking water standards have been promulgated at the federal level by the U.S.EPA. These standards would apply nationally to the quality of public drinking waters. For nine other parameters (Cl, Cu, Fe, Mn, Na, Ni, SO_4, U, and Zn), secondary standards related to broader water use concerns or health guidance levels have been suggested. Fourteen inorganic parameters assessed in Ohio brines (B, Ca, Co, CO_3, HCO_3, I, K, Li, Mg, Mo, P, SO_4, Sr, Ti, and V) have not been investigated for impact on drinking water quality in a manner that resulted in promulgation of water quality standards.

The U.S.EPA has begun evaluation of several inorganic chemicals in preparation for standard setting during the next three years. Therefore, for future reference on Ohio brine contaminants, the following parameters are currently under review for primary drinking water standards: Br, Cu, I, Mn, Mo, Ni, Sr, V, and Zn.

Several inorganic chemicals in Ohio brines are essential constituents of human genetic molecules, hormones, physiological fluids and proteins. During development of quality guidelines, much more complex interactions of the chemical with human nutrition as well as tolerance concentrations must be considered. Therefore, the U.S.EPA does not intend to establish standards over the next three years for the following: Ca, CO_3, HCO_3, K, Mg, and P.

The Wisconsin Department of Health and Social Services under that state's groundwater protection law has been charged with the task of establishing water quality standards for many existing and potential groundwater contaminants. For each chemical, an abbreviated risk assessment summarizes the following information:
  1. general chemical information;
  2. human exposure routes;
  3. acute toxicity;
  4. chronic toxicity;
  5. human health effects;
  6. mutagenicity;
  7. carcinogenicity;
  8. teratogenicity/reproductive effects;
  9. environmental fate;
  10. risk assessment;
  11. recommendations and conclusions;
  12. references.

Background information on the Wisconsin approach to these standards are included prior to the individual chemical reports. A table of all existing federal drinking water standards and reference to their full documentation are also included prior to the individual chemical reports.

Table 1. Summary of Health and Water Quality Standards on Inorganic
   Chemicals Identified in Ohio Brines.

Chemical	Standard	Source
Ag (Silver)	50 ug/l	WI (1985); U.S.EPA
As (Arsenic)	50 ug/l	WI (1985); U.S.EPA
B (Boron)	No Federal Standard	U.S.EPA (1986)
Ba (Barium)	1000 ug/l	WI (1985); U.S.EPA
Ca (Calcium)	No Federal Standard	U.S.EPA (1986)
Cd (Cadmium)	10 ug/l	WI (1985); U.S.EPA
Cl (Chlorine)	No Primary Standard Secondary Standard: 250,000 ug/l	U.S.EPA (1986)
Co (Cobalt)	No Federal Standard	U.S.EPA (1986)
CO_3 (Carbonate)	No Federal Standard	U.S.EPA (1986)
Cr (Chromium)	50 ug/l	WI (1985); U.S.EPA
Cu (Copper)	No Federal Standard Proposed Maximum Contaminant Level Goal: 1,300 ug/l	U.S.EPA (1986)
Fe (Iron)	No Primary Standard Secondary Standard: 300 ug/l	U.S.EPA (1986)
HCO_3 (Bicarbonate)	No Federal Standard	U.S.EPA (1986)
Hg (Mercury)	2 ug/l	WI (1985); U.S.EPA
I (Iodine)	No Federal Standard	U.S.EPA (1986)
K (Potassium)	No Federal Standard	U.S.EPA (1986)
Li (Lithium)	No Federal Standard	U.S.EPA (1986)

Standards reported as micrograms per liter (ug/l).

Sources: WI (1985); U.S.EPA: Standard established by the Wisconsin
Department of Health and Social Services and including an evaluation
of current and proposed U.S.EPA Drinking Water Standards either as
National Interim Primary Drinking Water Standards or as Maximum
Contaminant Levels.
      U.S.EPA (1986): evaluation of currently unregulated chemicals
as reported in personal communication with Ms. Jennifer Orme of the
U.S.EPA Office of Drinking Water October 31, 1986.

Table 1. Continued.

Chemical	Standard	Source
Mg (Magnesium)	No Federal Standard	U.S.EPA (1986)
Mn (Manganese)	No Primary Standard Secondary Standard: 50 ug/l	U.S.EPA (1986)
Mo (Molybdenum)	No Federal Standard	U.S.EPA (1986)
Na (Sodium)	No Federal Standard Health Guidance Level: 20,000 ug/l	U.S.EPA (1986)
Ni (Nickel)	No Federal Standard Health Guidance Level: 150 ug/l	U.S.EPA (1986)
P (Phosphorous)	No Federal Standard	U.S.EPA (1986)
Pb (Lead)	50 ug/l	WI (1985); U.S.EPA
Se (Selenium)	10 ug/l	WI (1985); U.S.EPA
SO4 (Sulfate)	No Federal Standard Health Guidance Level: 400,000 ug/l	U.S.EPA (1986)
Sr (Strontium)	No Federal Standard	U.S.EPA (1986)
Ti (Titanium)	No Federal Standard	U.S.EPA (1986)
U (Uranium)	No Federal Standard Health Guidance Level: 10 pCi/l	WI (1985); U.S.EPA
V (Vanadium)	No Federal Standard	U.S.EPA (1986)
Zn (Zinc)	No Primary Standard Secondary Standard: 5000 ug/l	U.S.EPA (1986)

Standards reported as micrograms per liter (ug/l); Uranium reported as picocurie units of radioactivity per liter (pCi/l)

Sources: WI (1985); U.S.EPA: Standard established by the Wisconsin Department of Health and Social Services and including an evaluation of current and proposed U.S.EPA Drinking Water Standards either as National Interim Primary Drinking Water Standards or as Maximum Contaminant Levels.
    U.S.EPA (1986): evaluation of currently unregulated chemicals as reported in personal communication with Ms. Jennifer Orme of the U.S.EPA Office of Drinking Water October 31, 1986.

TABLE

GROUNDWATER CONTAMINANTS FOR WHICH FEDERAL
MAXIMUM CONTAMINANTS LEVELS ARE ESTABLISHED

CATEGORY I

Parameter	Recommended Enforcement Standard (micrograms per liter except as noted)	References
Nitrate + Nitrite (as N)	10 mg/l	Federal Register, 40, 1975 (December 24) page 59570
Bacteria, Total Coliform	a) Membrane Filter: Coliform shall not exceed 1 per 100 ml. b) Fermentation Tube: Coliform shall not be present in any of the 10 ml. portions.	Federal Register, 40, 1975 (December 24) page 59571
Arsenic	50	Federal Register, 40, 1975 (December 24) page 59570
	50	Federal Register, 40, 1975 (December 24) page 59570
Chromium	50	Federal Register, 40, 1975 (December 24) page 59570
Lead	1 mg/l	Federal Register, 40, 1975 (December 24) page 59570
Barium		Federal Register, 40, 1975 (December 24) page 59570
Selenium	10	Federal Register, 40, 1975 (December 24) page 59570
Fluoride	2.2 mg/l	Federal Register, 40, 1975 (December 24) page 59571
2,4-Dichlorophenoxy- Acetic Acid	100	

TABLE

GROUNDWATER CONTAMINANTS FOR WHICH FEDERAL
MAXIMUM CONTAMINANTS LEVELS ARE ESTABLISHED

CATEGORY II

Parameter	Recommended Enforcement Standard (micrograms per liter except as noted)	References
Mercury	2	Federal Register, 40, 1975 (December 24) page 59570
Cadmium	10	Federal Register, 40, 1975 (December 24) page 59570
Methoxychlor	100	Federal Register, 40, 1975 (December 24) page 59570

CATEGORY III

Silver	50	Federal Register, 40, 1975, (December 24) page 59570
Toxaphene	.0007	USEPA, 1980 (EPA 440/5-80-076) page C 48-54
Endrin	.2	Federal Register, 40, 1975 (December 24) page 59570
2,4,5-Trichlorophenoxy-propionic Acid	10	Federal Register, 40, 1975 (December 24) page 59571
Lindane	.02	USEPA, 1980 (EPA 440/5-80-054) page C 34-36

Groundwater contamination by organic and inorganic chemicals, radionuclides, metals and/or microorganisms has occurred throughout the United States and is being detected with increased frequency. For many years the land surface and subsurface were considered safe areas for convenient disposal of waste and non-waste products. Recent evidence shows that soils containing disposal wastes possess limited capacities to metabolize contaminants into harmless products. Many toxic chemicals, rather than being changed into harmless compounds through natural soil processes, percolate unchanged through the soil and into aquifers. Although detailed quantitative estimates of the extent of groundwater contamination are unavailable, the presence of these chemicals in the nation's groundwater warrants national attention. Groundwater contaminants, especially organic chemicals, are associated with adverse social, environmental, economic, and health impacts.

Groundwater Contamination and Its Impacts

Groundwater is an important natural resource in the United States upon which Americans rely for about 50% of their drinking water supplies, 80% of rural domestic and livestock needs, about 40% of irrigation needs, numerous commercial activities, and almost 25% of self-supplied industrial needs (other than thermoelectric power). Groundwater is also used for stream flow maintenance, as a barrier to salt-water intrusion and is an intentional and unintentional depository for both waste and non-waste products.

The reliance of states and regions on groundwater supplies varies significantly in the United States. Groundwater used for public water supplies varies from 11% in the Great Lakes region to 75% in the Rio Grande region, for rural uses from 12% in Upper Colorado to 100% in New England, and for irrigation from 1% in the Upper Colorado to more than 90% in the Upper Mississippi.

Scientists believe that only a very small percentage of groundwater supplies are actually contaminated. However, contaminated aquifers are of significant public health concern because of their location under population centers and communities' reliance upon groundwater for drinking water.

Public concern due to groundwater pollution has focused upon the potential for causing adverse human effects. Lacking comprehensive estimates of groundwater quality in the United States or Wisconsin, it is impossible to accurately assess the magnitude and exact nature of the public health impacts of toxicant exposures from groundwater usage. Estimation of the potential human health impacts from exposure to individual contaminants is performed through the process of risk assessment. Risk assessment uses models of animal and human biological systems to estimate the likelihood of potential illnesses resulting from contaminant exposure. Information used in models to estimate human health impacts and propose health risk reduction regulatory limits on pollution levels include: adverse effects of a given compound (acute, chronic, carcinogenic, mutagenic, and teratogenic); the toxicity of a compound in terms of dosage level required to elicit an adverse health effect; exposure routes; the frequency the compound is found in groundwater; and the number of potentially exposed individuals. While data exists to perform some level of

risk analysis for most compounds, the information frequently lacks the precision needed to perform quantitative human health impact assessment. Human exposure data is usually non-existent and risk assessments must rely on extrapolating from high dose animal experiments to low dose human exposure. Data on individual human exposure to toxic substances in groundwater is almost totally lacking. Nearly insurmountable problems exist to conducting valid epidemiological investigations to detect incontrovertible human health impacts of groundwater pollution. It would be necessary to know, on an individual toxicant basis, the amount of exposure from groundwater alone (as opposed to exposure from air, food, and surface water), the number of persons exposed to various toxicant concentrations, and the health effects of multiple pollutant interactions when more than one toxicant is found in an aquifer.

While it is difficult to measure the lifetime health impacts of groundwater contamination, the nature of the contamination is known. Over 200 substances have been detected analytically in groundwater. Many of the chemicals are commonly used commercial, industrial and household products. Limited toxicological data is available for some of these compounds, including their adverse effects on animals and humans, toxicity levels, and ranges of contaminant concentrations in groundwater. However, a review of toxicological data from studies on laboratory animals, acute exposures to humans, quantitative human health studies conducted at the site of groundwater contamination, data on human health impacts of specific chemicals, and anecdotal information suggests that the consumption of chemically contaminated groundwater can result in acute, subchronic, and chronic human health impacts.

Substances found in groundwater are known to affect all organ systems but most commonly affect the central nervous system, liver, kidney, cause eye and skin irritation, and result in malignancies. The paramount factor determining whether damage could occur is the dose (amount) of the toxic agent present. The Office of Technology Assessment (OTA) lists the following chemicals as being associated with adverse health effects:

1. Liver, kidney, and central nervous system toxicants include: ethylbenzene and toluene (alkyl-substituted benzenes); carbon tetrachloride, chloroform and TCE (halogenated aliphatic hydrocarbons); bromobenzene, PBBs, and PCBs (halogenated aromatic hydrocarbons); chlordane, DDT, and toxaphene (chlorinated hydrocarbon pesticides); and some heavy metals.

2. Known or suspected carcinogens which have been found in groundwater include several aromatic hydrocarbons (benzene, benzidene, and MOCA), hydrocarbons with specific elements such as N,P,S,Cl,Br,I,F (aldrin, carbon tetrachloride, dichlorobenzidene, DDT, 1,2-Dichloroethane, 1,1-dichloroethylene, dieldrin, dioxins, Bis-2-ethylhexylphthalate, heptachlor, hexachloroethane, PCBs, simazine, tetrachloroethanes, 1,1,2-trichloroethylene, and vinyl chloride), and metals (antimony, barium, cadmium, chromium, and nickel).

3. Compounds found in groundwater which can damage the reproductive system or cause birth defects include DBCP, vinyl chloride, EDB, benzene, toluene, xylene, some chlorinated ethanes and phthalate esters, PCBs, and dioxins.

4. Some compounds found in groundwater might be expected to cause skin and eye irritation, particularly during bathing and showering. Available data suggests that these effects are reversible after cessation of exposure.

Some of the more recently identified contaminants of groundwater have not yet been fully investigated for their toxicity to animals and/or humans. Thus, toxicologists have been asked to develop guidelines determining the health and environmental effects of these toxicants to which humans may be currently exposed. In addition to the paucity of information on single toxicants, knowledge of possible interactions of combinations of groundwater contaminants is only now beginning to be studied in the laboratory. Groundwater contamination by several chemicals is a common occurrence. While toxicologists may be able to perform a valid health risk estimation when one chemical is present in groundwater, the presence of several compounds makes such estimations more complicated because the current levels of toxicological knowledge do not provide the information necessary to know if the interactions of several chemicals will cause an additive increase in toxicity (sum of the risks associated with each compound to obtain a total risk level), a synergistic effect (a toxic effect greater than the sum of the risks), an antagonistic effect (a toxic effect less than the sum of the risks), or no effect on the toxicity of a given compound.

The synergistic effects of several groundwater contaminants and alcohol ingestion have been documented. The liver toxicity of carbon tetrachloride, TCE and 1,1,1-trichloroethane is greatly increased in the presence of alcohol. The liver toxicity of TCE and PCE is also affected by Arochlor 1254, a PCB product.

Increasing the toxicological knowledge base for chemical pollutants is a national priority. While a great deal is known about many chemicals, there is always a need for additional, more precise and extensive studies. Until a data base is complete, the currently utilized risk assessment techniques guidelines are cautious. The dynamic nature of the growth in toxicological understanding means guidelines and standards will change to reflect the more precise data.

The Wisconsin Experience

The State of Wisconsin, with the passing of 1983 Wisconsin 410, has recognized the importance of groundwater protection and has mandated the Departments of Natural Resources and Health and Social Services to set groundwater toxicant enforcement standards. Groundwater provides nearly 70% of Wisconsin's drinking water and is the major source of water for industry and agriculture. Pesticides and Volatile Organic Chemicals (VOCs) are the two largest groups of man-made pollutants that have been found to contaminate groundwater.

Pesticides, applied to agricultural fields, can percolate down through the soil and enter groundwater as the original toxic pesticide or as toxic or non-toxic pesticide metabolites. The DNR's Groundwater Pesticide Sampling Program Summary for July 23, 1983 to June 25, 1984 reported aldicarb (Temik) as the predominant contaminant of Wisconsin groundwater with atrazine (Aatrex) a far second. Pesticides occasionally found in groundwater include metribuzin (Sencor), carbofuran (Furadan), chloramben (Amiben), dacthal metabolites,

dinoseb (Dinitro), metolachlor (Dual), butylate (Sutan+), alachlor (Lasso), and ethylenedibromide (EDB).

Volatile Organic Chemicals (VOCs) are common industrial and household chemicals which are being found in surface and groundwater. VOCs include metal degreasers, solvents, cleansers, and dry cleaning agents and have been used by gas stations, painting operations, metal fabricators and finishers, electronics firms and many other businesses.

Groundwater contamination by organic and inorganic chemicals, radionuclides, metals and/or microorganisms is occurring with increasing frequency throughout the United States. Whereas the disposal of chemicals in or on soils was once thought to result in the destruction or detoxification of these compounds, recent experience indicates that many toxic chemicals percolate through the soil and enter the groundwater unchanged or metabolized to products of equal or greater toxicity. Growing interest and awareness of the potential hazards associated with widespread groundwater contamination has resulted in the passing of legislation throughout the United States to control groundwater pollution. In Wisconsin, public recognition of the potential human and environmental health problems resulting from toxicant intrusion into groundwater used for purposes including drinking and food processing, led to the formulation of comprehensive groundwater protection legislation, 1983 Wisconsin Act 410, the so-called "Groundwater Bill."

Chapter 160 of the Groundwater Bill (Groundwater Protection Standards) requires Wisconsin regulatory agencies to submit to the Wisconsin DNR ". . . a list of those substances which are related to facilities, activities, and practices within its authority to regulate and which are detected in or have a reasonable probability of entering the groundwater of the state." The bill provides that substances can be placed in one of three categories: Category 1, if the substance is detected in groundwater in concentrations in excess of a federal number for that substance; Category 2, if the substance is detected in groundwater and is of public health or welfare concern but is not detected in concentrations in excess of a federal number or for which there is no federal number; and Category 3, if the substance has a reasonable probability of being detected in groundwater and is of public health or welfare concern. The bill also provides guidance for ranking the substances within each category. The DNR is instructed to give the highest rankings to those substances which pose the greatest risks to the health or welfare of persons in the state taking into consideration, among other things, the substances carcinogenicity, teratogenicity, mutagenicity, and interactive effects. The DNR may revise, as necessary, the ranking of substances within categories to include additional substances as they are reported, to reflect a change in the status of a substance which requires that it be moved either within or between categories, or to remove those substances from the list which are not shown to involve public health or welfare concerns or which do not have a reasonable probability of entering the groundwater.

The NR 140 approach to groundwater contaminant listing and evaluation provides state agencies with a solid management tool which is highly flexible yet provides firm guidelines for the categorization of contaminants of concern. Flexibility is of great importance due to the dynamic nature of the toxicological literature and the finding of new contaminants in the

groundwater from time to time. Without the flexibility to add, subtract or move a contaminant within or between categories, it would be difficult for state agencies to respond to changing technical knowledge and field experience within a reasonable time frame. Additionally, the ability to move a contaminant within a category permits agency staff to prioritize and review the toxicology of a compound on a schedule which responds to the needs of the public for information and guidance in evaluating the potential human health and environmental effects a substance.

Protecting the groundwater from contamination is of great concern because of the serious social, economic, environmental and human health implications should substance concentrations reach unacceptable levels. The State of Wisconsin is expanding groundwater monitoring for chemical contaminants and is evaluating the potential human health effects of groundwater contamination. DNR, with the toxicological assistance of DHSS, has established enforcement standards as required by 1983 Wisconsin 410 for the 36 compounds which follow. A brief toxicological summary as well as the rationale for each proposed standard is provided for each substance.

Two public hearings were held on January 14 and 16, 1985, in Madison and Stevens Point, respectively, concerning the creation of ch. NR 140, Wis. Adm. Code, relating to the development and implementation of groundwater quality standards. An additional hearing was held on February 14, 1985, in Madison, to respond to questions on how the standards were developed and to make further comments on the proposed standards. The effective date of NR 140, the rules establishing the standards, is October 1, 1985. These rules are authorized by s. 144.025(2) and ch. 160 Stats. A continuing program of toxic substance evaluation by DHSS and DNR will result in the subsequent establishment of groundwater pollutant enforcement standards for additional chemicals. The public hearing draft of ch. NR 140, Wis. Adm. Code, proposed the establishment of enforcement standards and preventive action limits for radioactive substances and for trihalomethanes. Following the public hearings, the Department of Natural Resources did not proceed with the adoption of an enforcement standard and a preventive action limit for trihalomethanes because that was a class of substances rather than a single substance. As of this writing, the enforcement standards and preventive action limits for radioactive substances (beta particle and photon radioactivity; radium 226 and 228; uranium) have not been published in NR 140. The Department of Health and Social Services is proceeding first with the adoption of groundwater standards for radioactive substances pursuant to s. 140.56(2), Wisconsin Statutes. The information on radioactive substances contained in the background document prepared for the public hearings is contained in Appendix V.

References:

Protecting the Nation's Groundwater from Contamination.
(Washington, D.C.: U.S. Congress, Office of Technology Assessment, OTA-233, October, 1984). 244 p.

Groundwater Pesticide Sampling Program Summary, DNR, Transmitted November 28, 1984

SILVER

Introduction:

Silver is a white, ductile metal occurring naturally in its pure form and in ores, most commonly argentite. It is principally used as an electroconductor, in photographic materials, electroplating, dental alloys, solder and brazing materials, paints, jewelry, silverware, coinage and mirrors. Silver nitrate, 1-2% silver by weight, is used medicinally in the prophylaxis of ophthalmia neonatorum. Silver has been used to purify water and is found in fresh water at average concentrations of 0.2 µg/liter. Some U.S. surface waters had concentrations of silver from 0.1 to 38 µg/liter. Finished water in U.S. cities had trace levels of silver to 7 µg/liter (mean of 2.3 µg/liter). One study found silver in tap water from public water supplies as high as 26 µg/liter. No silver has been detected in Wisconsin Community water systems.

Human Exposure Routes:

Silver may enter the human body via ingestion of contaminated water and food, through inhalation, or dermally. Estimated intake of silver in food is approximately 70 µg/day. Silver is a very minor constituent of ambient aerosols. Dermal contact generally results from the application of silver-containing medication.

Acute Toxicity:

The following values were found in the literature:

*Intraperitoneal LD_{50} (mice): 13.9 mg/kg (silver nitrate)

Acute toxic effects of silver in animals is usually associated with intravenous administration of silver nitrate which causes symptoms including pulmonary edema, weakness, rigidity, contractures in the legs, loss of voluntary movements, and interference with cardiac blood supply.

Chronic Toxicity:

No data were available for review.

Human Health Effects:

Metallic silver is not regarded as a toxic compound, whereas most of its salts are toxic to numerous organisms. These salts can combine with certain biological molecules to cause toxicity. Ingestion of silver results in the additive deposition of silver in the skin and mucous membranes. Generalized or localized argyria, primarily involving the eyes, is the most common noticeable effect of chronic and subacute human exposure to silver or silver compounds. Argyria is most commonly caused by medicinal applications of silver compounds and industrial exposure. The minimum accumulation of silver thought to present a risk of argyria is 1 gm.

Mutagenicity:

Silver was not found to be mutagenic in the Ames test, or in _Micrococcus aureus_.

Carcinogenicity:

Studies involving implanted foils, disks, or injected suspensions or metallic silver have produced tumors or hyperplasia, but the interpretations of these studies has been questioned. No definite links between human cancer and silver as the causative agent have been established.

Teratogenicity/Reproductive Effects:

Few associations between silver and birth defects have been reported in the literature.

Environmental Fate:

Sorption and precipitation processes reduce the concentration of dissolved silver and result in higher concentrations of the element in bed sediments than in the overlying waters. Some silver may be bioaccumulated.

Risk Assessment:

Silver compounds have not been found to be mutagenic, carcinogenic or teratogenic. EPA regulates silver as part of the _National Interim Drinking Water Regulations_. The EPA MCL is .05 mg/l.

Recommendations and Conclusions:

Until further information on chronic animal feeding studies, which would allow the determination of a reliable NOEL, and the subsequent development of a standard based upon the procedures outlined in ss 160.07(4) and 160.13, the Department of Health and Social Services recommends adopting the EPA MCL as the groundwater enforcement standard (.05 mg/l or 50 µg/l).

Recommended Enforcement Standard: 50 µg/liter (50 ppb)
Recommended Preventive Action Limit factor: 20%

References:

General: USEPA, 1980. _Ambient Water Quality Criteria for Silver._ Office of Water Regulations and Standards, Criteria and Standards Division. Springfield, VA

Federal Register, 40, 1975 (December 24) page 59570

ARSENIC

Introduction:

The three types of arsenical compounds formed from elemental arsenic are inorganic arsenic, organic arsenic, and arsine gas.[1] Common arsenic compounds include arsenic pentoxide, arsenic trioxide, sodium arsenate, and sodium aresenite, all of which are soluble in water. The source of approximately 97% of all arsenic products is arsenic trioxide or white arsenic. Pentavalent organic arsenicals are used for animal medications. Elemental arsenic and arsenic compounds are used in pesticides, glass ceramics, paints, dyes and hide preservation. About 70 million pounds of arsenic and inorganic arsenic compounds are produced in the U.S. annually with over 95% of the arsenic produced as a byproduct of copper or lead smelting.[2]

Arsenic as a free element can be encountered in natural waters, with the thermodynamically more stable inorganic arsenate perdominating over arsenite in water. The low toxicity of elemental arsenic is attributed to its relative insolubility in water or in body fluids. Arsenic is commonly found in U.S. waters including surface waters where concentrations ranged from less than 10 to 1,100 µg/liter (median <10 µg/liter). Arsenic concentrations in U.S. river waters averaged less than 10 µg/liter with 22% of the samples having concentrations of 10-20 µg/liter. Lassen County, California reported arsenic concentrations in well water ranging from 0.1 mg/liter or less to 1.4 mg/liter. Arsenic has been detected in 11 Wisconsin community water system samples at concentrations of 11-29 ppb during the period from 1981 – 1984.[3] Natural sources, such as the erosion of surface rocks, probably account for a significant portion of arsenic found in surface and groundwater. Arsenic is found in the earth's crust at concentrations averaging 2 ppm and is concentrated in shales, clays, phosphorites, coals, sedimentary iron ore and manganese ores.

Human Exposure Routes:

Industrial workers can be exposed to arsenic and its compounds during manufacture and processing operations. Approximately 545,000 workers are potentially exposed to arsenic, with higher than average worker exposure occurring in the smelting of arsenic containing ores and during pesticide application. Food consumption may provide an intake of about 0.02 mg/day/ person of arsenic compounds. Trace levels of arsenic have been found in tissues of livestock treated with arsenical medications and feed additives. Arsenic exposure can also occur through the consumption of contaminated drinking water. Air emissions of arsenical compounds from pesticide manufacturing facilities, cotton gins, glass manufacturing operations, and other sources can expose the general population to these materials. EPA estimates total environmental emissions at 9,000 pounds a year.[4]

Acute Toxicity:

Typical systemic manifestations of arsenic poisoning due to ingestion include gastrointestinal disturbances with the intensity of effects due to the type and quantity of arsenical ingested. Acute poisoning often begins with a feeling of throat discomfort which is followed by difficulty in swallowing, epigastric discomfort and violent abdominal pain accompanied by vomiting and

diarrhea. Other symptoms are intense thirst, muscle cramps, and systemic collapse which may result in cardiac failure. Subacute symptoms are less intense.

Chronic Toxicity:

Long-term exposure to arsenic via ingestion of food, water or medication have resulted in vague abdominal symptoms such as diarrhea or constipation, flushing of the skin, pigmentation, and hyperkeratosis. Chronic exposure to arsenic has been reported to cause various malignancies, gastrointestinal distress, paresthesis, dermatological problems, vascular disorders, and death.

Human Health Effects:

Severe toxicosis can result in humans who ingest arsenic-contaminated food or drink. The symptoms of severe arsenic poisoning are profound gastrointestinal damage and cardiac abnormalities. Other health problems associated with arsenic exposure include vomiting, diarrhea, conjunctivitis, rhinitis, laryngitits, bronchitis, skin eruptions, abnormal skin pigmentation, hoarseness, hyperesthesias, paresthesias, neuralgias, muscle tenderness, motor weakness of all degrees, congestive heart failure, and nail changes.

Mutagenicity:

Chromosomal breaks in human leukocyte cultures have been reported after short term _in vitro_ and long term _in vivo_ exposures to arsenical compounds. Arsenic compounds have been shown to cause chromosome breakage in numerous biological systems. Phytohemagglutinin-stimulated lymphocyte cultures were prepared for psoriasis patients who received arsenic treatments at one time during their therapy. The incidence of chromosomal aberrations was remarkably greater in the cultures of patients who were exposed to arsenic than the control group. Analysis of short-term cultured leukocytes from arsenic exposed mine workers showed that chromosomal aberration among these workers was significantly higher than control groups.

Carcinogenicity:

Information on the carcinogenicity of arsenic and arsenic compounds in experimental animals is considered inadequate for evaluation. Sufficient evidence exists that skin cancer in humans is causally associated with exposure to inorganic arsenic compounds in drugs, drinking water, and occupational environments.[2] IARC concluded that while inadequate evidence for the carcinogenicity of arsenic compounds in animals exists, there is sufficient evidence that inorganic arsenic compounds are skin and lung carcinogens in humans.[5] Lung cancer risks in certain smelter workers who inhaled high levels of arsenic trioxide showed a 4-12 fold increase over non-exposed individuals. Case reports have suggested an association between arsenic compound exposure and blood dyscrasias and liver tumors.[2]

Teratogenicity/Reproductive Effects:

Several studies show that sodium arsenate induces developmental malformations in hamsters, rats and mice. Pregnant golden hamsters injected with sodium arsenate at 15 to 25 mg/kg b.w. produced offspring with malformations

including anencephaly, renal agenesis, rib malformation, and cleft lip and palate. Intraperitoneal injections of sodium arsenate in pregnant mice produced an increase in fetal resorptions, a significant decrease in fetal weights, and malformations including exencephaly, shortening of the jaws with consequent protrusion of the tongue, exophthalmos, missing pinna, cleft lip, hydrocephalus, umbilical hernia, ectrodactyly, micromelia, and shortened or twisted tail, limb, or both.

Environmental Fate:

No data were available for review.

Risk Assessment:

Arsenical compounds have been determined to be mutagens, carcinogens and teratogens. The National Interim Primary Drinking Water Regulations for arsenic are .05 mg/l.[6] However, this did not fully consider the carcinogenic properties of arsenic. A carcinogen risk assessment was performed by the EPA-CAG and they determined that the lifetime cancer risk at 10^{-6} occurred at a water concentration of .000002 mg/l (2 ppt).

Recommendations and Conclusions:

During the public comment period, DNR and DHSS received from the USEPA a current staff review of the existing interim arsenic MCL which is being used in the preparation of EPAs proposed RMCLs.[7] Unlike the 1976 Interim Primary Drinking Water Regulations, the current review recognizes the carcinogenicity of arsenic. The review concludes that the existing MCL of 50 µg/l provides adequate protection and allows for the possibility that arsenic may be an essential element at very low levels.

Based on this new information, it appears unlikely that the final EPA RMCL will be substantially lower than the existing MCL. Given this information, DHSS now feels that it is appropriate to utilize the 1976 MCL as the federal number upon which Wisconsin groundwater standards should be based.

Because arsenic is a human carcinogen, and ss. 160 does not stipulate that classification as a carcinogen only pertains to carcinogenicity via the water route, DHSS recommends that the PAL factor remain at 10%.

> Revised Recommended Enforcement Standard: 50 µg/l (50 ppb)
> Recommended Preventive Action Limit factor: 10%

References:

1. International Labour Office, 1983. Encyclopedia of Occupational Health and Safety. International Labour Organization. Geneva.

2. USDHHS, 1983. Third Annual Report on Carcinogens - Summary. Public Health Service. Springfield, VA. p. 22-24

3. DNR Personal Communication. December, 1984.

4. National Research Council, 1977. _Drinking Water and Health_.
    National Academy Press. Washington, D.C. Vol. 1, p. 316-318

5. National Research Council, 1983. _Drinking Water and Health_.
    National Academy Press. Washington, D.C. Vol. 5, p. 118-123

6. USEPA, 1976. _National Interim Primary Drinking Water Regulations_.
    p. 54

7. USEPA, 1984. Proposed RMCLs: Inorganic and Synthetic Organic
    Chemicals and Microbiological Contaminants. p. 72

General: USEPA, 1980. _Ambient Water Quality Criteria for Arsenic_.
          Office of Water Regulations and Standards, Criteria and
          Standards Division. Springfield, VA. (EPA 440/5-80-021)

          Federal Register, _40_, 1975 (December 24) page 59570

PUBLIC COMMENTS FROM NR 140 HEARINGS AND AGENCY RESPONSES:

COMMENT: The proposed 2 micrograms/liter enforcement standard for
arsenic and 30 micrograms/liter for cadmium are unreasonable and
impractical. Setting the proposed enforcement standard for chromium at
half the current EPA standard for chromium is unwarranted. (Source:
WAMC, Merlin Horn, PW&L)

RESPONSE: During the public comment period for ch. NR 140, DNR and DHSS
received from the USEPA a current staff review updating the existing
interim maximum contaminant level (MCL) for arsenic, which is being used
in the preparation of EPAs proposed RMCLs. Unlike the 1976 Interim
Primary Drinking Water Regulations, the current review recognized the
carcinogenicity of arsenic.

The review concludes that the existing MCL of .05 mg/l for arsenic
provides adequate protection and allows for the possibility that arsenic
may be an essential element at very low levels. Based on this new
information, it appears unlikely that the final EPA RMCL will be
substantially lower than the existing MCL. Therefore, DHSS now feels
that it is appropriate to utilize the 1976 MCL as the federal number upon
which Wisconsin groundwater standards should be based. Because arsenic
is a human carcinogen, and ch. 160, Stats., does not stipulate that
classification as a carcinogen only pertains to carcinogenicity via the
water route, DHSS recommends that the PAL be set at 10%.

Introduction:

Barium is abundant in the environment and accounts for 0.04% of the earth's crust. The chief sources of barium are the minerals barite (barium sulphate) and witherite (barium carbonate). Barium metal is produced in limited quantities by aluminum reduction of barium oxide in a retort and is little used by industry.[1] Barium occurs naturally in almost all (99.4%) surface water examined at concentrations of 2-340 µg/liter with an average of 43 µg/liter. Lowest concentrations of barium are in the western Great Lakes (15 µg/liter) and highest in the southwestern drainage basins of the lower Mississippi Valley (90 µg/liter). Barium has been detected in 6 Wisconsin community water system samples at concentrations of 500-1,400 ppb during the period from 1982 to 1984.[2] Finished water of public systems frequently contains barium ranging from 1-172 µg/liter (mean=28.6 µg/liter). The 100 largest U.S. cities had median concentrations of 43 µg/liter. Drinking water at the tap exceeded the interim standard in only 2 of 2,595 samples.

Human Exposure Routes:

Human exposure occurs through ingestion of drinking water, by inhalation of barium dusts, and by accidental ingestion.

Acute Toxicity:

No data were available for review.

Chronic Toxicity:

Male and female weanling rats were given 5 mg/liter barium acetate in drinking water over their lifetimes. No toxicity was observed in terms of survival times or effect on growth rate. Minor changes were seen in fasting serum glucose and cholesterol values and an increase in proteinuria in males was reported. Rats given barium chloride in drinking water at concentrations ranging from 0-250 mg/liter for 4, 8 and 13 weeks only developed a slight decrease in adrenal gland weights.[3]

Human Health Effects:

Barium metal has limited usage and is mainly an explosion hazard. The soluble compounds of barium (chloride, nitrate, and hydroxide) are highly toxic. Inhalation of the insoluble sulphate compounds may give rise to pneumoconiosis. Many of the barium compounds, including the sulphide, oxide, and carbonate may cause local irritation to the eyes, nose, throat, and skin.[1] Acute barium poisoning exerts a strong, prolonged stimulant action on all muscles including the cardiac and smooth muscle of the gastrointestinal tract and bladder. Barium is also capable of causing nerve blockage, and in small or moderate doses can produce a transient increase in blood pressure by vasoconstriction. No determination has been made on the chronic effects of barium administered repeatedly over long periods of time in either food or drinking water.[4] Studies on the effects of elevated barium levels in drinking water found male deaths from cardiovascular disease and female deaths from all causes significantly higher than control groups.[3]

Mutagenicity:

No data were available for review.

Carcinogenicity:

No data were available for review.

Teratogenicity/Reproductive Effects:

No data were available for review.

Environmental Fate:

No data were available for review.

Risk Assessment:

Insufficient data was found to assess the potential of barium for mutagenicity, carcinogenicity, or teratogenicity. The EPA has regulated barium in drinking water through the National Interim Primary Drinking Water Regulations.[5] After review of the toxicologic (animal and human) data, EPA established an MCL of 1 mg/l for barium.

Recommendations and Conclusions:

Until additional information becomes available, the Department of Health and Social Services recommends adopting the EPA MCL for barium of 1 mg/l as the groundwater enforcement standard.

Recommended Groundwater Enforcement Standard: 1 mg/l (1 ppm)
Recommended Preventive Action Limit factor: 20%

References:

1. International Labour Office. 1983. Encyclopedia of Occupational Health and Safety. International Labour Organization. Geneva

2. DNR Personal Communication. December 1984

3. National Research Council, 1982. Drinking Water and Health. National Academy Press. Washington, D.C. Vol. 4, p. 167-170

4. National Research Council, 1977. Drinking Water and Health. National Academy Press. Washington, D.C. Vol. 1, p. 229-231

5. Federal Register, 40, 1975 (December 24) page 59570

CADMIUM

Introduction:

Cadmium is a silvery-white metal that is used principally by industry in electroplating, in the manufacture of pigments, as a plasticizer, in batteries, and in electrical conductors. While not abundant, cadmium is found wherever zinc is found in nature. Cadmium in the environment comes from industrial sources. Unpolluted fresh water contains concentrations of cadmium at around 1 μg/liter.[1] Cadmium has been detected in 52 Wisconsin community water system samples at concentrations of 0.3-1.5 ppb during the period from 1981 to 1984.[2]

Human Exposure Routes:

While cadmium may be consumed in drinking water, the major source of cadmium for the general populace is in the diet. Average daily intakes range from 50 to 150 μg/day with water accounting for 5% or less. Cigarette smoke contains about 1 ppm cadmium, so those who smoke one pack of cigarettes daily are exposed to 2 to 4 μg of cadmium per day. Occupational exposures to cadmium are considerable, averaging around 0.02 to 0.05 mg/m^3. Ambient air is not a significant source of cadmium exposure for the majority of the U.S. population.[1]

Acute Toxicity:

The following values have been reported in the literature:

* Oral LD_{50} (rats): 175-225 mg/kg
* Oral LD_{50} (rats): 72 mg/kg (oxide)
* Oral LD_{50} (rats): 88 mg/kg (chloride)
* Oral LD_{50} (rats): 100 mg/kg (fluorosilicate)

High doses of cadmium in test animals caused testicular necrosis, structural and functional changes in the liver, tubular damage in the kidneys, and hemorrhagic lesions of sensory ganglia in the central nervous system.[1]

Chronic Toxicity:

Male rats exposed to cadmium concentrations ranging from 10-100 mg/liter for 24 weeks showed renal injury at the 30 and 100 mg/liter dosage levels. Male rats fed cadmium in their drinking water at 250 mg/liter for 2 or 8 weeks had alterations in hepatic and renal cytochrome P-450 levels.[3] Immunosuppression, moderate anemia, and hypertension have been reported in experimental animals treated with cadmium.

Human Health Effects:

Cadmium is a very toxic element, exposure to which can cause acute or chronic toxicity in humans. The ingestion of cadmium-contaminated foods and fluids can produce acute toxic effects manifested as gastrointestinal disturbances such as nausea, vomiting, pain, diarrhea and tenesmus. Acute effects of industrial exposure are manifested as lung damage with symptomatology

including chest pain and pulmonary edema, which may result in death. Chronic occupational cadmium exposure causes obstructive lung disease and renal dysfunction. Chronic cadmium exposure may act as a predisposing factor in hypertension.[3]

Mutagenicity:

Little information exists on the mutagenicity of cadmium. Mice exposed to cadmium were reported to have an increase in the incidence of dominant lethal mutations. In two studies of human lymphocyte cultures exposed to cadmium, one report noted chromosome damage while the other did not.[3]

Carcinogenicity:

Evidence for the carcinogenicity of cadmium and certain cadmium compounds in experimental animals is sufficient, while such evidence in humans is limited. Cadmium chloride, oxide, sulfate, and sulfide given subcutaneously to rats caused local sarcomas. Local sarcomas were seen in rats following intramuscular injection with cadmium powder and cadmium sulfide. Testicular tumors were produced in rats and mice following subcutaneous administration of cadmium chloride and cadmium sulfate. Occupational exposure studies have suggested that cadmium in some form (possibly the oxide) increases the risk of prostate, respiratory, and genitourinary cancers in humans.[4]

Teratogenicity/Reproductive Effects:

Parenterally injected cadmium induces teratogenic effects in laboratory rats, mice, and hamsters including dose-related increases in fetal deaths, decreases in fetal weight, increased rate of anomalies such as micrognathis, cleft palate, club foot, small lungs, encephaly, spina bifida, absence of tail, and malformations of the ribs, skull, and vertebrae.[3]

Environmental Fate:

Cadmium has been found to bioconcentrate in human food items in aquatic food chains.

Risk Assessment:

Cadmium has demonstrated mutagenic, carcinogenic, and teratogenic activity. The EPA included cadmium in the National Interim Primary Drinking Water Regulations but the calculated MCL did not include evaluation of carcinogenicity.[5] The EPA did complete a carcinogen risk assessment which determined the water concentration which would result in a 10^{-6} lifetime cancer risk. The 10^{-6} cadmium in water concentration was .00003 mg/l.

Recommendations and Conclusions:

During the public comment period, DNR and DHSS received from the USEPA a current staff review updating the existing 1976 cadmium Interim MCL which is being used in the preparation of EPAs proposed RMCLs. Unlike the 1976 Interim Primary Drinking Water Regulations, the current review recognizes the carcinogenicity of cadmium. The proposed RMCLs discussed in the USEPA

document are closer to the existing MCL than to the 1980 Ambient Water Criteria Document carcinogen risk assessment produced by EPA upon which DHSS had based its recommended enforcement standard. Should the EPA final RMCL for cadmium differ substantially from the existing MCL which DHSS will now utilize as the most appropriate federal number for this recommended enforcement standard, DHSS will review the EPA RMCL and evaluate whether to accept this new number as its groundwater standard.

Since the USEPA will shortly complete its review and development of a proposed RMCL for cadmium, DHSS now feels that it is most appropriate to utilize the 1976 MCL of .01 mg/l as the federal number upon which Wisconsin groundwater standards should be based.

Because cadmium is an animal carcinogen, and ss. 160 does not stipulate that classification as a carcinogen only pertains to carcinogenicity via the water ingestion route, DHSS recommends that the PAL factor remain at 10%.

    Revised Recommended Enforcement Standard: 10 µg/l (10 ppb)
    Recommended Preventive Action Limit factor: 10%

References:

1. National Research Council, 1980. Drinking Water and Health. National Academy Press. Washington, D.C. Vol. 3, p. 91-96

2. DNR Personal Communication. December, 1984

3. National Research Council, 1982. Drinking Water and Health. National Academy Press. Washington, D.C. Vol 4, p. 170-174

4. DHHS, 1983. Third Annual Report on Carcinogens. Public Health Service. Springfield, VA. p. 36-37

5. USEPA, 1976. National Interim Primary Drinking Water Regulations. Page 59

General: USEPA, 1980. Ambient Water Quality Criteria for Cadmium. Office of Water Regulations and Standards, Criteria and Standards Division. Springfield, VA. (EPA 440/5-80-025)

        Federal Register, 40, 1975 (December 24) page 59570

PUBLIC COMMENTS FROM NR 140 HEARINGS AND AGENCY RESPONSES:

COMMENT: The proposed 2 micrograms/liter enforcement standard for arsenic and 30 micrograms/liter for cadmium are unreasonable and impractical. Setting the proposed enforcement standard for chromium at half the current EPA standard for chromium is unwarranted. (Source: WAMC; Merlin Horn, PW&L)

RESPONSE: During the public comment period for ch. NR 140, DNR and DHSS received from the USEPA a current staff review updating the existing

interim maximum contaminant level (MCL) for cadmium, which is being used
in the preparation of EPAs proposed RMCLs. Unlike the 1976 Interim
Primary Drinking Water Regulations, the current review recognized the
carcinogenicity of cadmium.

The proposed RMCL discussed in the USEPA document for cadmium is closer
to the existing MCL than to the carcinogen risk assessment presented by
EPA in 1980 Ambient Water Criteria Document and upon which DHSS based its
Recommended Enforcement Standard. Should the EPA final RMCL for cadmium
substantially from the existing MCL which DHSS now proposes utilizing as
the most appropriate federal number for the recommended enforcement
standards, DHSS will review the EPA RMCL and evaluate whether to adopt
this new number as its groundwater standard. Since the EPA will shortly
complete its review and development of the proposed RMCLs for cadmium,
DHSS feels that it is appropriate to utilize the 1976 MCLs of .01 mg/l
for cadmium as the enforcement standards. Because cadmium is an animal
carcinogen, DHSS recommends that the PAL factor be 10% for cadmium.

TOTAL CHROMIUM

Introduction:

Chromium is a metallic element, commonly found in low concentrations in the environment, which may exist in several valence states. In the aquatic environment it is usually found in the +3 or +6 valence state, and it is the trivalent and hexavalent chromium compounds which are of biological and environmental concern. Hexavalent chromium is very soluble in water and is relatively stable in most natural water. In a 1975 paper, it was noted that, due to the possibilities for oxidation of chromium III and the reduction of chromium VI, water quality standards should be based on total chromium rather than on hexavalent chromium. Large amounts of hexavalent chromium are produced and utilized by industry (primarily as chromates and dichromates), and it is therefore expected that traces such water-soluble compounds should be found in natural waters. In 1972 approximately 320,000 metric tons of the metal were used by U.S. industry. Although found in the continental crust at 125 mg/kg, chromium is rarely found in natural water. Several studies of chromium in drinking water found mean concentrations of 9.7 and 7.5 µg/liter and a median concentration of 0.43 µg/liter.[1] Chromium has been detected in 43 Wisconsin community water system samples at concentrations of 5-37 ppb during the period from January to September of 1984.[2]

Human Exposure Routes:

Total dietary intake of chromium is estimated at 50-100 µg/day. Chromium may be inhaled from urban, nonurban, or industrial air. Cutaneous exposure is primarily a problem of the workplace.

Acute Toxicity:

The following values have been reported in the literature:

*Intravenous LD$_{50}$ (no animal designated): 10 mg/kg

Chronic Toxicity:

Chromium in the form of K_2CrO_4, administered to dogs for four years at 0.45 mg/liter in drinking water, showed no pathology. Chromium compounds fed to laboratory animals have been reported to cause rough and dirty coat, sterility, and general sub-normal conditions in rats, as well as dose-dependent decreases in liver and spleen weights. Available data indicates that few systemic changes would be expected to result from even moderately elevated oral chromium exposures. However, high concentrations of chromium injected into animals has caused renal damage.

Human Health Effects:

Acute and chronic toxicity in humans is a problem associated with industrial environments or areas polluted by industrial sources. Adverse health effects caused by human exposure to chromium include systemic actions and primary lesions of the skin, respiratory passages, and the lungs. High concentrations of chromium cause renal damage, including tubular necrosis. Besides ulcerative skin changes due to contact exposure to various compounds, persons