INORGANIC CHEMICALS INCLUDING RADIOACTIVE MATERIALS IN WATERBODIES

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Summary

Most of the inorganic chemicals contained in aquatic environments are heavy metals, inorganic anions and radioactive materials. Therefore, the WHO guidelines for drinking water quality recommend values for 18 inorganic substances. Radioactive constituents are also recommended for gross alpha activity and gross beta activity.

Inorganic contamination of aquatic environments is caused by naturally occurring substances (fluoride, arsenic and boron), industrial waste (mercury, cadmium,

chromium, cyanide and others), agricultural and domestic waste (nitrogen compounds), and systems for the distribution of drinking water (aluminum, copper, iron, lead and zinc). Naturally occurring inorganic materials mainly contaminate groundwater; industrial and agricultural waste, mainly surface water such as rivers, lakes and ponds; and pipes of distribution systems, mainly tap water.

Each of the inorganic substances contaminating water has a characteristic nature, concentration in water and effect on human health.

1. Introduction

Most inorganic chemicals polluting aquatic environments are heavy metals, inorganic anions and radioactive materials. This pollution is caused by naturally occurring substances such as fluoride, arsenic and boron, by industrial waste containing mercury, cadmium, chromium, cyanide and others, by agricultural and domestic waste containing nitrogen compounds, and from contamination by copper, iron, lead and zinc during the distribution of drinking water.

Naturally occurring inorganic substances mainly contaminate groundwater, whereas industrial and agricultural waste contaminates surface water such as rivers, lakes and ponds. The major source of contamination in drinking water is the distribution system. WHO guideline for drinking water quality recommended values for 18 inorganic substances. (Table 1)

Compounds	**Guideline value (mg/L)**	**Remarks**
Antimony	0.018	
Arsenic	0.01 (P)	For excess skin cancer risk of $6x10^{-4}$
Barium	0.7	
Boron	0.01 (P)	
Cadmium	0.003	
Chromium	0.05	
Copper	2 (P)	
Cyanide	0.07	
Fluoride	1.5	*
Lead	0.01	**
Manganese	0.5	
Mercury(total)	0.001	
Molybdenum	0.07	
Nickel	0.02	
Nitrate(as NO_3^-)	50	***
Nitrite(as NO_2^-)	3	***
Selenium	0.01	
Uranium	0.009 (P)	

(P) : Provisional guideline value

* : Climatic conditions, volume of water consumed, and intake from other sources should be considered when setting national standards

** : It is recognized that not all water will meet the guideline value immediately; meanwhile, all other recommended measures to reduce the total exposure to lead should be implemented

*** : The sum of the ratio of the concentration of each to its respective guideline value should not exceed 1

Table 1: WHO drinking water guidelines inorganic constituents

Values are also recommended for radioactive constituents such as gross alpha activity (0.1 Bq L^{-1}) and gross beta activity (1 Bq L^{-1}).

This chapter describes the main substances contaminating water based on WHO guidelines.

2. Naturally Occurring Substances in Bodies of Water

Inorganic substances sometimes affect human health or ecological systems when eluted from the earth's crust into water. In many cases, materials such as arsenic, fluoride and boron are contained in groundwater; however, sometimes they flow to the surface of the earth as spring water.

2.1. Arsenic

Arsenic is a metalloid widely distributed in the earth's crust and present at an average concentration of 2 mg kg^{-1}. Arsenic can exist in four valency states; -3, 0, +3, and +5. Under reducing conditions, arsenite (As (III)) is the dominant form; arsenate (As (V)) is generally the stable form in oxygenated environments. Elemental arsenic is not soluble in water. Arsenic is used commercially and industrially as an alloying agent in the manufacture of transistors, lasers, and semiconductors, as well as in the processing of glass, pigments, textiles, and wood preservative.

Arsenic is also used in the hide tanning process and in pesticides, and pharmaceuticals. Arsenic is widely distributed in surface water, with concentrations in rivers and lakes generally below 10 μg L^{-1}. Arsenic levels in groundwater average about 1-2 μg L^{-1} except in areas with volcanic rock and sulfide mineral deposits where they can reach up to 3 mg L^{-1}. Concentrations of arsenic in the open ocean are typically 1-2μg L^{-1}. However, there have been a number of reports of higher than usual concentrations of arsenic in well water. Under natural conditions, the greatest range and highest concentrations of arsenic are found in groundwater as a result of the influence of rocks such as arsenopyrite (FeAsS). Chronic arsenic disease caused by arsenic-contaminated well water has been reported in various countries. Recent epidemiological study has revealed that a total of about 1 billion people; 47 million in India (West Bengal) and Bangladesh, 3 million in China, 0.3 million in Chile, and various numbers in other countries (i.e. Thailand, Nepal, Vietnam, Cambodia, Mexico, and Argentina) use arsenic-contaminated wells for drinking water, and this total is increasing year by year.

However, it is not clear what the situation is in Africa, Central Asia and the Middle East because there has been no epidemiological study. Individuals developed chronic arsenic disease after drinking contaminated well water (about 0.5 mg L^{-1} As) for 5 to 6 years (average) or after drinking highly contaminated water (3- 5 mg L^{-1} As) for several months. Long-term exposure to arsenic in drinking water is causally related to an increased risk of cancer in the skin, as well as other effects on skin such as hyperkeratosis and changes in pigmentation. The Incidence of skin cancer is now being studied in Bangladesh, India, Chile and China.

Table 2 summarizes naturally occurring arsenic problems in groundwater reported from IPCS of WHO in 2001. In this report, arsenic was detected in groundwater at concentration of 176-5300 μg L^{-1}, and the population exposed ranged from 500 to 3 x 10^7. The WHO recommends 0.01mg L^{-1} for drinking water quality provisional guideline value. In a number of countries, this value has been adopted as a standard. However, many countries have retained the earlier WHO guideline of 0.05 mg L^{-1} as a national standard or as a target value.

Country/Region	**Concentration Range (μg/L)**	**Area (km^2)**	**Population exposed**
Bangladesh	<0.5-2500	150,000	Ca. 3×10^7
West Bengal	<10-3200	23,000	6×10^6
Taiwan	10-1820	4,000	10^5
Inner Mongolia	<1-2400	4,300	?
China (Xinjiang)	40-750	38,000	500
Hungary	<2-176	110,000	29,000
Argentina	<1-5300	100,000	2×10^6
Northern Chile	100-1000	125,000	5×10^6
South west USA	<1-2600	5,000	3×10^5
Mexico	8-620	32,000	4×10^4

(IPCS ,EHC No.224 Arsenic 2001)

Table 2: Summary of naturally occurring As problems in groundwater

Countries that have adopted 0.01mg L^{-1} as the standard include members of EU(1998), Japan(1993), Jordan(1991), Laos(1999), Mongolia(1998) and Namibia, and Syria(1994). Countries that have adopted other values are as follows; Australia (0.007 mg L^{-1},1996), Canada(0.025mg L^{-1},1999), and USA(0.005 mg L^{-1}, 1986 proposed). Countries where the national standard for arsenic in drinking water remains at 0.05 mg L^{-1} include Bahrain, Bangladesh, Bolivia (1997), China, Egypt(1995), India, Indonesia(1990), Oman, Philippines(1978), Saudi Arabia, Sri Lanka(1983) Vietnam(1989) and Zimbabwe.

2.2. Boron

Boron is a naturally occurring element that is found in the form of borates in the ocean, sedimentary rocks, coal, shale, and some soils. It is widely distributed in nature, with a concentration of about 10 mg kg^{-1} in the Earth's crust (range: 5mg kg^{-1} in basalts to 100 mg kg^{-1} in shales) and about 4.5 mg L^{-1} in the ocean.

Boron is widely distributed in the environment, borax, kemite, and tourmaline being three of the more commonly mined boron minerals. The chemical forms of boron in nature include boric acid and more condensed species such as tetra-borate.

Elemental boron and its carbides are used in high-temperature abrasives, special-purpose alloys, and steel-making. Boron hydrides are used as reductants, to control heavy metal discharges in waste-water, as catalysts. Boric acid and borates are used in the manufacture of glass and as wood and leather preservatives and cosmetic products. Boric acid, borates, and perborates have been used as mild antiseptics or bacteriostats in eyewashes and mouthwashes. Borax is used extensively as a cleaning compound, and borates are applied as agricultural fertilizers.

Boron enters the environment mainly through the weathering of rocks, boric acid volatilization from seawater, and volcanic activity. Boron is also released from anthropogenic sources such as agricultural refuse, and from wood burning, the manufacture of glass, the use of borates/perborates in the home and industry, borate mining/processing, and sewage/sludge disposal.

Borate ions present in aqueous solutions are essentially in a fully oxidized state. No aerobic processes are likely to affect their speciation, and no biotransformation processes are reported.

The concentration of boron in seawater ranges from 4 to 5 mg L^{-1} as boric acid. Also naturally occurring boron is present in groundwater primarily as a result of leaching from rocks and soils containing borates and borosilicates. The concentration of boron in groundwater throughout the world ranges widely, from <0.3 to >100 mg L^{-1}. The amount of boron in surface water depends on the geochemical nature of the drainage area, proximity to marine coastal regions, and inputs from industrial and municipal effluents. Concentrations in surface water are summarized in Table 3.

Area	**Boron concentration (mg/L)**
USA	0.076 (median) , 0.387 (90th percentile)
Drainage basins	0.019-0.289
Coastal drainage waters	15 (boron-rich deposits)
lakes	157-360 (boron-rich deposits)
Canada, Ontario	0.029-0.086
river water	0.063
United Kingdom	0.046—0.822
Italy	0.4-1.0 (range of mean), <0.1-0.5
Sweden	0.013- (0.001-1.046)
Germany	0.02-2.0
Netherlands	0.09-0.145 (range of medians)
Austria, river waters	<0.02-0.6
Russia, river waters	0.01-0.02
Pakistan	<0.01-0.46 (near effluent discharges)
Turkey, river waters	<0.5 (uncontaminated), 4 (boron mine waste)

Argentina	<0.3, 6.9 (near borate plant)
Chile, river waters	3.99-26 (soil rich in minerals and natural salts)
Japan, river waters	0.009-0.012
South Africa	0.02-0.33

(IPCS,EHC No.204 Boron 1998)

Table 3: Concentration of boron in surface water

Concentrations in surface waters in North America (USA, Canada) ranged from 0.02 mg L^{-1} to as much as 360 mg L^{-1}. Concentrations ranged from 0.001 to 2 mg L^{-1} in Europe, with mean values typically below 0.6 mg L^{-1}. Similar concentrations have been reported for bodies of water within Pakistan, Russia, and Turkey; from <0.01 to 7 mg L^{-1}, with most values below 0.5 mg L^{-1}. In Japan, concentrations of boron in surface water ranged up to 0.1 mg L^{-1} and in South Africa up to 0.3 mgL^{-1}. Typical boron concentrations were less than 0.1 mg L^{-1}, with 90% of samples containing approximately 0.4 mg L^{-1}. In rain and snow, boron was found at 0.0031 to 0.0056 mg L^{-1}, respectively at six sites in western Switzerland.

Chronic exposure to boric acid and borax leads to gastrointestinal and kidney problems with loss of appetite, nausea, and vomiting, and the appearance of an erythematous rash. Boron is suspected to be an endocrine disrupter based on results of animal experiments in which it caused severe testicular atrophy and spermatogenic arrest.

2.3. Fluoride

Fluorine is a common element that does not occur in an elemental state in nature because of its high reactivity. It accounts for about 0.3 g kg^{-1} of the earth's crust and exists in the form of fluorides in a number of minerals, of which fluorite, cryolite, and fluorapatite are the most common. The oxidation state of the fluoride ion is -1. Inorganic fluorine compounds are used in industry for a wide range of purposes. They are used in aluminum production and as a flux in the steel and glass fiber industries. They can also be released into the environment during the production of phosphate fertilizers (which contain an average of 3.8% fluorine), bricks, tiles, and ceramics. For dental purposes, fluoride preparations may contain low concentrations of fluoride (1000-1500mg per kg of toothpaste). Fluoride levels in surface waters vary according to geographical location and proximity to emission sources. Surface water concentrations generally range from 0.01 to 0.3 mg L^{-1}. Ambient surface water fluoride levels are summarized in Table 4.

Location	**Fluoride concentration (mg/L)**
Areas with low natural fluoride	
Canada	0.05
USA	0.035-0.052 (<0.001-0.59)
Belgium, river waters	0.13-0.2
France, river waters	0.08-0.25
Norway, lakes waters	0.037 (<0.005-0.56)
Spain, river waters	0.1
United Kingdom, river waters	<0.05-0.4

streams	0.02-0.22
Nigeria, river waters	0.1-0.12
India, river waters	0.2-0.25
river waters	0.038-0.21
China, river waters	0.04
Japan,	>1
Areas with high natural fluoride	
USA、hot springs	20-50
river waters	1-14
lakes	>13
Kenya, lakes	>2800

(IPCS, EHC No.227 Fluoride 2002)

Table 4: Concentration of fluoride in unpolluted water

Concentrations of fluoride in surface waters of North America ranged from 0.035 to 0.05 mg L^{-1}. Concentrations ranged from <0.05 to 0.56 mg L^{-1} in Europe, with similar concentrations reported for water bodies within Nigeria, India and China. Higher levels of fluoride have been measured in areas where the natural rock is rich in fluoride and near industrial outfalls. For example, in Norwegian lakes, concentrations ranged from <0.005 to 0.56 mg L^{-1}, with a mean value of 0.037 mg L^{-1}. Elevated inorganic fluoride levels in surface water are often seen in regions where there is geothermal or volcanic activity. The most well documented area of high-fluoride surface water associated with volcanic activity follows the East African Rift Valley system. Many of the lakes of the Rift Valley system have extremely high fluoride concentrations—for example, 1640 and 2800 mg L^{-1}, respectively, in the Kenyan lakes. In seawater, a total fluoride concentration of 1.3 mg L^{-1} has been reported.

Fluoride is probably an essential element for humans and animals. Fluoride is an important element and where there are elevated intakes through drinking water, sometimes in conjunction with other sources, crippling skeletal fluorosis, can occur in addition to the adverse cosmetic effects of dental fluorosis. Many epidemiological studies of possible adverse effects of the long-term ingestion of fluoride via drinking water have been carried out. These studies clearly establish that fluoride primarily produces effects on skeletal tissues (i.e. bones, teeth). Low concentrations provide protection against dental caries, especially in children. This protective effect, which is associated with surface contact with enamel, increases with concentration up to about 2 mg L^{-1} of drinking water; the minimum concentration of fluoride in drinking water required to produce it is approximately 0.5 mg L^{-1}. However, fluoride also can have an adverse effect on tooth enamel and may give rise to mild dental fluorosis at drinking water concentrations between 0.9 and 1.2 mg L^{-1}.

Elevated fluoride intakes can also have more serious effects on skeletal tissues. Skeletal fluorosis is observed when drinking water contains 3-6 mg L^{-1} of fluoride. Crippling skeletal fluorosis usually develops where drinking water contains over 10 mg L^{-1} of fluoride.

3. Inorganic Substances in Industrial Waste

Many inorganic substances are used for industrial manufacturing. Pollution of the water environment occurs from industrial manufacturing and the use of these products. Many kinds of metals contaminate water via waste water and sludge from industrial factories, mines or smelting stations. Metals related to the contamination of water are as follows; antimony, arsenic, barium, beryllium copper, iron, zinc, cadmium, chromium, manganese, nickel, selenium, mercury, uranium and others. Main inorganic substances related to water pollution and health effects are described.

3.1. Antimony

Antimony is used in semiconductor alloys, batteries, antifriction compounds, cable sheathing, flameproofing compounds, ceramics, glass, pottery, type castings for commercial printing, solder alloys and fireworks. Antimony has been identified in natural waters in both the antimony (III) and antimony (V) oxidation states and as methyl antimony compounds. It occurs in seawater at a concentration of about 0.2µg L^{-1}. A survey in the USA found antimony in only three of 988 samples of drinking water from groundwater sources, the concentrations ranging from 41 to 45µg L^{-1}. In a study of 3834 samples of drinking water, antimony was found in 16.5%, at concentrations ranging from 0.6 to 4 µg L^{-1}. Workers exposed for 9-31 years to dust containing a mixture of antimony trioxide and antimony pentoxide in an antimony smelting plant exhibited symptoms such as chronic coughing, bronchitis, emphysema, conjunctivitis, and staining of the teeth. Antimony dermatitis was seen in more than half of the exposed workers.

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