Copper

The aesthetic objective for copper in drinking water is *≤1.0 mg/L*; this was set to ensure palatability and to minimize staining of laundry and plumbing fixtures. Copper is an essential element in human metabolism, and it is well-known that deficiency results in a variety of clinical disorders, including nutritional anaemia in infants. Although the intake of large doses of copper has resulted in adverse health effects, the levels at which this occurs are much higher than the aesthetic objective.

General

Copper occurs in nature as the metal and in minerals, most commonly cuprite (Cu_2O) and malachite ($Cu_2CO_3(OH)_2$). The principal copper ores are sulphides, oxides, and carbonates.(1)

Copper has been known, mined, and used by humans for more than 5000 years. It is probably second only to iron in its usefulness to humans. Copper pipe is used extensively in plumbing, especially for domestic water systems. Copper is used in the production of electrical wire and in the manufacture of alloys such as brass and bronze.(1,2) It is also used in electroplating, in photography, as roofing, as a catalyst in the chemical industry, and for the removal of mercaptans in oil refining.(3,4) Copper is used extensively in pesticide formulations as a fungicide and antimicrobial agent, particularly for the treatment of wood and water supplies for drinking water and recreational use.

In 1981, the world production of copper from mines was 8.30 million tonnes. Canada ranked fourth, with 8.33 percent of the total production. The 1981 world production of refined copper was 9.69 million tonnes. Canada ranked sixth, producing 0.477 million tonnes.(5) In 1975, Canadian copper mine production was concentrated in Ontario (36.6 percent), British Columbia (33.3 percent), Quebec (16.3 percent), and Manitoba (8.9 percent).(1)

Occurrence

Copper may occur as the metal and in oxidation states as copper(I) and copper(II). An unstable copper(III) is also known. In aqueous solution, copper is present mainly as the copper(II) ion, depending on pH, temperature, the presence of bicarbonate and sulphide, and the potential to form ligands with organic species, such as humic, fulvic, and amino acids, certain polypeptides, and detergents.(6) The free copper(I) ion can exist in aqueous solution only in exceedingly low concentrations, and the only copper(I) compounds that are stable in water are the highly insoluble ones, such as chloride or cyanide.(7) Some copper(II) salts, including the chloride, nitrate, and sulphate, are soluble at low pH under oxidizing conditions. The carbonate, hydroxide, oxide, and sulphide are less soluble, particularly at pH 7 or higher. In alkaline waters with high carbon dioxide content, copper may precipitate as copper carbonate.(8)

Copper and its compounds are widely distributed in nature, and copper is found frequently in surface water and in some groundwater. Based on NAQUADAT data on copper concentrations in Canadian surface and lake waters from 1980 to 1983, extractable copper levels ranged from 0.001 to 0.080 mg/L, with concentrations rarely exceeding 0.005 mg/L.(9) Surveys of Canadian drinking water supplies in 1976 and 1977 provided information on copper levels in raw water supplies from rivers, lakes, and wells, treated drinking water at the treatment facility, and distributed water at the consumer's tap(10) (Table 1). In another national survey, the median copper concentration in distributed water was 271 µg/L (range <10 to 900 µg/L) for 27 supplies with acid or neutral pH (90% with pH 5.3 to 7.5).(11) In general, the ratio of copper concentrations in distributed and treated water was about 10 to 1 but ranged from 1.6 to over 100 to 1.

Table 1. Copper concentrations in Canadian drinking water supplies(10)

Water source	Raw water (µg/L)		Treated water (µg/L)		Distributed water (µg/L)	
	Mean	Range	Mean	Range	Mean	Range
River	≤5	≤5–530	≤5	≤5–100	20	≤5–220
Lake	≤5	≤5–80	≤5	≤5–100	40	≤5–560
Well	≤5	≤5–110	≤5	≤5–70	75	10–260

Distributed water contains considerably more copper than the original water supply because of the dissolution of copper from copper piping, which is used extensively in domestic plumbing in Canada. Soft waters with low pH, low alkalinity, and low conductivity are often more corrosive than hard waters, but these factors alone cannot be used to predict the degree of metal mobilization. Eleven water chemistry variables—potassium, sodium, calcium, magnesium, manganese, chloride, nitrate, hydrogen, sulphate, dissolved oxygen, and conductivity—were all related to the degree of elevation of copper in the water.[12]

Because the length of time that the water stands in the pipe is also important, the most relevant data for determining actual copper intake are copper concentrations in consumed water. In an integrated monitoring survey carried out in seven Ontario communities selected as representative of soft, medium, and hard water supplies with high, moderate, or low aggressiveness, six homes in each community were equipped with a sampler attached to the kitchen tap, which sampled all water used throughout the day. The copper concentration in consumed water over a one-week sampling period averaged 176 µg/L (range 20 to 2020 µg/L). Ninety percent of all levels measured were below 300 µg/L.[13]

Levels of copper in a range of foodstuffs are listed in Table 2. Some foods, such as shellfish (especially oysters), organ meats, nuts, dried beans, dried vine and stone fruits, and cocoa, are particularly rich in copper. The copper content of these items can range from 20 to 400 µg/kg.[14] Dairy products, white sugar, and honey rarely have copper concentrations above 0.5 µg/kg, and non-leafy green vegetables, most fresh fruits, and refined cereals generally contain copper at levels up to 2 µg/kg.[14] Some of the highest levels of copper can be found in tree nuts and certain condiments and spices, such as black pepper, thyme, and yeast.[14]

Table 2. Mean copper levels in foods[14]

Food type	Concentration (µg/kg wet weight)
Seafood (finfish and shellfish)	1.49
Meat (poultry, pork, beef, lamb)	3.92
Dairy (eggs, milk, butter)	1.76
Vegetables (leafy, beans, root crops)	1.17
Fruits (tree fruits including tropicals)	0.82
Grains and cereals	2.02
Oils and fats	4.63
Nuts	14.82
Condiments and spices	6.76
Beverages (including wine, beer, spirits)	0.44

Although it has been suggested that it is difficult to prepare a diet of natural foods that provides less than 2 mg of copper per day,[14] which is the level considered to be adequate for normal copper metabolism,[15] a recent review of copper requirements concluded that the modern American diet often provided less than this, in the range of 1 mg/day.[16] Many processed foods (i.e., "fast" foods) common in North American diets are very low in copper content.[17]

No data are available on copper concentrations in air in Canada. Nriagu calculated the average range of copper concentrations in rural and urban air to be 0.005 to 0.05 µg/m^3 and 0.03 to 0.2 µg/m^3, respectively,[18] too low to be a source of concern.

Canadian Exposure

Using a value of 0.176 mg/L, the average concentration of copper consumed in drinking water as obtained from the integrated monitoring survey in Ontario, one can estimate the daily intake of copper from tap water to be 0.264 mg for an adult consuming an average of 1.5 L of water per day.

Various estimates of the copper intake from a typical Canadian diet have been made. Daily copper consumption in Vancouver in 1970 and in Toronto in 1971 was estimated to be 2.1 mg.[19] In a cross-Canada study, it was concluded that the average individual ingested 2.2 mg of copper per day.[20]

Assuming that ambient urban air containing copper concentrations ranging from 0.03 to 0.2 µg/m^3 is inhaled by a 70-kg person breathing 20 m^3 of air per day, the copper intake through inhalation would be 0.01 to 0.06 µg/kg body weight per day.

Average daily exposures from air, food, and water for a person weighing 70 kg, drinking 1.5 L of water per day, and inhaling 20 m^3 of air per day are summarized in Table 3.

Table 3. Average daily exposures from air, food, and water

	Exposure		
Route	mg/day	%	mg/kg body weight per day
Air	0.00070–0.004	0.16	0.00001–0.00006
Food	2.200	89.14	0.0314
Water	0.264	10.70	0.00377
Total	2.468*	100.00	0.0352*

* Assuming maximum exposure through air.

Analytical Methods and Treatment Technology

In the past, the most commonly employed methods for copper analysis were atomic absorption spectrometry (AAS) and atomic emission spectrometry (AES).[21] Using these methods, the lowest detection limit was 0.001 mg/L, but a practical quantitation limit of about 0.01 mg/L was the norm. More recently, inductively coupled plasma excitation (ICP) methods, such as ICP–AES and ICP–mass spectrometry (ICP–MS), have begun to replace the older ones.[22,23] The detection limit for ICP–AES is 0.001 mg/L,[23] but for ICP–MS the limit tends to vary according to the composition of the sample in question.

Treatment processes for the control of copper in water may be based on removal from the raw water supply or alteration of the water chemistry to reduce corrosivity.[24] Copper may be removed by coagulation with aluminium or ferric salts; 98% removal was predicted at pH 8, depending on the concentration of organic complexing agents.[25] The average copper reduction in 12 conventional water treatment plants in California and Colorado was 49%, whereas other tests found no reduction in copper after conventional treatment.[24] Lime precipitation followed by settling was effective in copper removal; treatment of a solution with an influent concentration of 0.1 mg/L resulted in a finished concentration of less than 0.001 mg/L.[26] More advanced treatment processes, such as reverse osmosis and distillation, are also effective in removal of copper.

Conditioning of water to prevent dissolution of copper from plumbing materials is recommended in view of the significance of this source of copper in domestic water supplies. The U.S. Environmental Protection Agency (EPA) recommends that communities whose tap water contains high copper levels should raise the pH above 8 and the alkalinity to 30 mg/L or more.[16]

Health Considerations

Essentiality

Copper is an essential element in mammalian nutrition and is required in many enzymatic reactions. It is essential for the normal utilization of iron, because of the requirement of ferroxidase (ceruloplasmin) for iron transport. Copper deficiency (less than about 2 mg/day) is accompanied by anaemia, resulting from the inability of reticulocytes to obtain iron from transferrin and to synthesize haem from iron(III) and protoporphyrin at a normal rate.[27] Other copper-requiring enzyme systems include monoamine oxidase enzymes, required for pigmentation and control of neurotransmitters and neuropeptides; lysyl oxidase, essential for the maintenance of connective tissue in lungs, bone, and elastin in the cardiovascular system; cytochrome c oxidase, involved in oxidative metabolism, brain functioning, haem synthesis, and phospholipid synthesis; and superoxide dismutase, required for the destruction of superoxide radicals.[28]

The ratio of copper to other dietary components (e.g., zinc, iron, sulphate, and molybdenum) may be as important as the actual copper levels in the diet.[29] Copper/zinc ratios may be important to the adequate metabolism of cholesterol, with low ratios resulting in hypercholesterolaemia.[17,30]

Severe copper deficiency has been observed in malnourished children in Peru. Symptoms included anaemia, neutropenia, and disturbances of bone formation, which responded to copper supplementation.[31] Patients on parenteral alimentation for various medical reasons have also shown signs of copper deficiency.[28] Experimentally induced copper deficiency in a 29-year-old male, caused by consuming a diet that contained only 0.8 mg of copper per day for 105 days, resulted in abnormal electrocardiograph values (premature ventricular beats). Similarly, cardiovascular disturbance, including a heart attack, severe tachycardia, and extrasystolic beats, resulted from administration of diets containing only 1 mg of copper per day (0.35 mg/1000-kcal diet) to 29 male volunteers.[32] In adults, these results indicate that the observed signs of cardiovascular-related dysfunctions may be more sensitive indicators of copper deficiency than anaemia.[28]

Metabolism

Based on studies with radioactive isotopes of copper, most copper is absorbed from the stomach and duodenum of the gastrointestinal tract. Maximum blood copper levels were observed within 1 to 3 hours following oral administration, and about 50 percent of ingested copper was absorbed.[17] Copper absorption is proposed to occur by two mechanisms, one energy-dependent and the other enzymatic. Factors that can interfere with copper absorption include competition for binding sites with zinc, interactions with molybdenum and sulphates, chelation with phytates, and inhibition by ascorbic acid.

Copper absorbed from the gastrointestinal tract is transported rapidly to blood serum and deposited in the liver bound to metallothionein, from which it is released and incorporated into ceruloplasmin, a specific copper-transporting protein. Copper that remains in the serum is bound to albumin or amino acids or is contained in the erythrocytes. About 80 percent of the absorbed copper is bound to liver metallothionein; the remainder is incorporated into cytochrome c oxidase or sequestered by lysosomes.[17]

The distribution of copper is affected by sex, age, and the level of copper in the diet. Brain and liver have the highest tissue levels (about one-third of the total body burden), with lesser concentrations found in the heart, spleen, kidneys, and blood. The iris and choroid of the eye have very high copper levels.[17]

Erythrocyte copper levels are very stable, whereas plasma levels fluctuate widely in association with the synthesis and release of ceruloplasmin. Plasma copper levels during pregnancy may be two to three times levels before pregnancy, due to the increased synthesis of ceruloplasmin. The source of the extra copper appears to be the liver. Oestrogens appear to be the stimulatory agents for the release of copper from the liver, as oestrogen treatment is associated with increased plasma copper levels in both men and women. Oral contraceptives cause marked increases in serum copper levels.[17]

Metabolic balance studies demonstrate that persons with daily intakes of 2 to 5 mg of copper per day absorbed 0.6 to 1.6 mg (32%), excreted 0.5 to 1.3 mg in the bile, passed 0.1 to 0.3 mg directly into the bowel, and excreted 0.01 to 0.06 mg in the urine.[28] As these data indicate, urinary excretion plays a minor role in copper clearance, and the principal route of excretion is in the bile. Other minor excretory routes include saliva, sweat, menstrual flow, and excretion into the intestine from the blood.[28]

The biological half-life for copper clearance from the body is very short (i.e., hours); therefore, copper would not tend to accumulate in the body.[17]

Adverse Effects

Acute copper poisoning is rare in higher mammals owing to the potent emetic action of copper. In humans, acute copper toxicity has usually been associated with accidental consumption; symptoms include a metallic taste in the mouth, nausea, vomiting, epigastric pain, diarrhoea, jaundice, haemolysis, haemoglobinuria, haematuria, and oliguria. In severe cases, the stool and saliva may appear green or blue; in the terminal phases, anuria, hypotension, and coma precede death.[17,33]

Ingestion of more than 15 mg of copper has been reported to be toxic to humans.[34] In a survey of human clinical case studies, 5.3 mg/day was the lowest oral dose at which local gastrointestinal irritation was seen.[35,36] Ingestion of gram quantities of copper sulphate resulted in death by suicide, whereas less severe effects were reported from estimated copper doses of 40 to 50 mg from ingestion of carbonated beverages in contact with copper containers.[8]

Limited data are available on the chronic toxicity of copper. The hazard from dietary intakes of up to 5 mg/day appears to be low.[8] Two groups are at increased risk from the toxic effects of chronic ingestion of high doses: individuals with glucose-6-phosphate (G-6P) dehydrogenase deficiencies, and individuals with Wilson's disease, an inborn error of copper metabolism in which copper accumulates in the brain, liver, and kidney.[28] An infant who was fed water containing copper at 6.8 mg/L for 14 months was reported to have died, but it was not known whether he suffered from one of the genetic conditions mentioned above.[8]

Wide variation has been reported in the susceptibility of different animal species to copper. Sheep appeared to be one of the most sensitive species because of a deficiency of G-6P dehydrogenase;[8] rats were one of the least sensitive. Swine showed hypochromic microcytic anaemia, jaundice, and marked increases in liver and serum copper levels at the copper concentration of 750 µg/g diet. A level of 250 µg/g diet was toxic to swine unless supplementary zinc and iron were included. No toxicity was observed for animals with diets containing copper at 750 µg/g when the animals received zinc and iron supplements of 500 to 750 µg/g diet.[28,37]

Signs comparable to hepatic haemosiderosis developed in swine and rats with chronic dietary excesses of copper. The applicability of these data to humans was questioned, as excess copper ingestion in humans was seldom associated with hepatic haemosiderosis.[38]

The International Agency for Research on Cancer has not evaluated copper or copper compounds for carcinogenicity. An increased incidence of granulomas in the liver and malignant lung tumours has been reported in vineyard workers in France, Portugal, and Italy who were exposed to copper sulphate sprays mixed with lime to control mildew.[39,40] Quantitative estimates of the levels of copper exposure could not be made from these data.[17] The U.S. EPA has classified copper compounds in Group D—inadequate data in humans and animals.[36]

Copper compounds were reported to be negative in microbial mutation assays.[36] No other data were available on results of short-term *in vitro* or *in vivo* genotoxicity tests.

No data were available on teratogenic effects of copper. Copper deficiency during pregnancy was reported to result in poor fertility in sheep and cattle.[28]

Recommended Daily Intake

The World Health Organization has recommended a daily intake of 30 µg/kg body weight per day (or 2.1 mg/day) for an adult male and 80 µg/kg body weight per day for infants.[41] These recommendations were based on balance studies in children and adults, including studies on intakes required to equal the daily copper loss through metabolism and excretion. The recommendations for adults are similar to those (2 to 3 mg/day) of the National Academy of Sciences. Intakes as low as 5.3 mg/day have been reported to be mildly toxic, but most reports of toxicity involve intakes of 15 mg/day or more.

Other Considerations

The presence of copper in domestic water systems has caused green staining of laundry and plumbing fixtures at concentrations as low as 1.0 mg/L.[42] Temperature, aggressive tendencies of water, and impurities in copper piping all contribute to the solvency of copper and consequently to the staining problem. Dissolved copper can also have a detrimental effect on galvanized products, as it enhances the corrosion of aluminium and zinc.

Copper in water has an unpleasant, astringent taste. The taste threshold for copper in distilled water is in the range of 2.4 to 3.2 mg/L.[43,44] In carbonated mineral water from the former West Germany, the taste threshold for copper was 0.8 to 1.0 mg/L,[43] whereas it was 5 mg/L in Arkansas, USA.[44]

Conclusions

1. Copper is an essential and beneficial element in human metabolism. Its recommended daily intake, based on essentiality, is about 2 mg/day for adults, or 30 µg/kg body weight per day. At average concentrations, drinking water contributes approximately 11% of the daily copper requirement. Copper is generally considered to be non-toxic except at high doses, in excess of 15 mg/day.

2. Copper in public water supplies enhances corrosion of aluminium and zinc. It also imparts an undesirable bitter taste to water. Staining of laundry and plumbing fixtures occurs at copper concentrations above 1.0 mg/L.

3. The aesthetic objective for copper in drinking water is therefore ≤1.0 mg/L. This level is below the taste threshold for copper in water, is protective of health, and contributes to minimum nutritional requirements.

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