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WATER QUALITY OFFICE

THE IMPACT OF VARIOUS METALS ON THE AQUATIC ENVIRONMENT

BY

Robert F. Schneider

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INVESTIGATIONS - DENVER CENTER

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SYNOPSIS: A literature review of the effects of arsenic, copper, cadmium, lead and zinc species on water quality and aquatic biota is presented. Some synergistic and antagonistic effects are discussed and the existing governmental standards for these metals are summarized.

ARSENIC (As)

Water Quality

Arsenic is a normal constituent of most soils, with concentrations ranging up to 500 mg/kg. In its elemental form, arsenic is insoluble in water, but many of the arsenates are highly soluble. Most, if not all, natural waters contain arsenic compounds. Its natural occurrence is very common in the freshwater of the western United States (McKee and Wolf, 1963). Elsewhere (i.e., New Zealand) lethal doses of arsenic (20 mg/animal lb.) have been recorded as occurring naturally in freshwater (Grimmett and McIntosh, 1939).

Through domestic water supplies arsenic compounds are constantly taken into the human body where they are cumulative. Human blood normally contains 0.2 to 1.0 mg/l of arsenic (Browning, 1961).

In seawater, normal arsenic concentrations are recorded to be 0.003 mg/l (Lambou and Lim, 1970a.) As mentioned above, arsenic compounds are cumulative in living tissue. Thus, in the sea, marine plants (i.e., brown algae) have been found to contain concentrations up to 30 mg/l (FWPCA, 1968). Arsenic is also commonly found in marine animals. According to the work of Vinogradov (1953), it accumulates up to 0.3 mg/l in some molluscs, coelenterates, and crustaceans. McKee and Wolf (1963) report that shellfish may contain over 100 mg/kg.

Biotic Response

Arsenic is notorious for its toxicity to humans. Ingestion of as little as 100 mg usually results in severe poisoning and as little as 130 mg has proved fatal (Browning, 1961).

Several incidents have demonstrated that arsenic in water may be carcinogenic. Cancer of the skin and possibly of the liver is attributed to arsenic in drinking water (Arguello, et. al., 1960; Kathe, J., 1937; Tello, E. E., 1951).

Some bioassay work has been done with arsenic, but the results are not based on standard testing methods such as the 96 hour TL_m (see McKee and Wolf, 1963 p. 141 for detailed bioassay results).

It is interesting to note that arsenic concentrations of 3-20 mg/l have not harmed aquatic insects such as immature dragonflies, damselflies, and mayflies (Rudolfs, et. al., 1950).

Rudolfs (1944) also reported that concentrations of 2-4 mg/l of arsenic did not interfere in any way with the self-purification of streams.

Standards

Most State codes do not specifically cite metals, so the statement made here will probably apply to all the metals discussed herein. Governmental water quality codes often briefly define hazardous metals and for abatement purposes the common code statement is ". . . no toxic materials (metals, often understood) in concentrations that will impair the usefulness of receiving waters as a source of supply or interfere with other legitimate use of said waters".

To summarize limits for arsenic in water, as suggested by various agencies, refer to the following table.

TABLE 1. Arsenic (As) Concentration (mg/l)

Arsenic Concentration	Organization & Date of Recommendation	Comment
0.05	USPHS, 1942	Maximum permissible concentration in drinking water.
0.05	USPHS, 1946	Maximum permissible concentration in drinking water.
0.2	W.H.O., 1958	Maximum allowable concentrations for potable water.
0.2	W.H.O. European, 1961	Tolerance limit for drinking water standards.
0.01	USPHS, 1962	Recommended limit for drinking water.
0.05	USPHS, 1962	Maximum allowable limit for drinking water.
0.05	State of California, 1963	Maximum limit for domestic water supplies.
1.0	State of California, 1963	Maximum limit for irrigation water supplies.
1.0	State of California, 1963	Maximum limit for stock and wildlife watering.
1.0	State of California, 1963	Maximum limit for fish and other aquatic life waters.
0.05	State of Texas, 1967	Maximum limit for inland waters.
1.0	State of Texas, 1967	Maximum limit for tidal waters.
0.05	State of Colorado (date unknown)	Maximum allowable limit for surface waters to be used for public water supply - after complete treatment.
0.05	State of Florida (date unknown)	Maximum allowable for surface waters in Florida.
0.05	State of Illinois (date unknown)	Maximum allowable limit for surface waters used for public supply - after complete treatment.

Arsenic Concentration	Organization & Date of Recommendation	Comment
0.05	State of Indiana (date unknown)	Maximum allowable limit for surface waters used for public supply - after complete treatment.
0.05	State of Iowa (date unknown)	Maximum allowable limit for surface waters used for public supply - after complete treatment.
0.01	State of Minnesota (date unknown)	Maximum allowable limit for surface waters used for public supply - after complete treatment.
0.05	State of Mississippi (date unknown)	Maximum allowable limit for surface waters used for public supply - after complete treatment.
0.05	State of Alaska (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
0.05	State of Connecticut (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
0.05	State of Maine (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
0.05	State of Michigan (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
0.05	State of Montana (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
0.05	State of Nevada (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
0.05	State of Ohio (date unknown)	Maximum allowable limit for surface waters used for public supply - after complete treatment.
0.05	State of Rhode Island (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
0.05	State of Vermont (date unknown)	Same as USPHS, 1962, Drinking Water Standards.

COPPER (Cu)

Water Quality

Metallic copper is insoluble in water, but many copper salts are highly soluble as cupric or cuprous ions. Copper (cupric) ions are not likely to be found in natural surface or groundwaters. This is because as they are introduced into natural waters of pH7, or above, these ions quickly precipitate and are thereby removed by adsorption and/or sedimentation (McKee and Wolf, 1963).

In natural freshwater, copper salts occur in trace amounts, up to about 0.05 mg/l (McKee and Wolf, 1963). In seawater, copper is found at a level of 0.003 mg/l. Therefore, the presence of greater amounts of copper salts is generally the result of pollution, attributable to the corrosive action of the water on copper pipes, to industrial discharges, or frequently to the use of copper compounds for the control of undesirable algae.

Copper is not considered to be a cumulative systemic poison, like lead or mercury. In humans, most of the copper ingested is excreted by the body and little is retained. In lower organisms there is some record of accumulation. Marine animals have been found to contain 4 to 50 mg/l and in some sponges accumulation has exceeded these values (FWPCA, 1968).

Biotic Response

In concentrations high enough to be dangerous to humans, copper renders a disagreeable taste to the water. Threshold concentrations for taste have been reported in the range of 1.0 - 2.0 mg/l of copper, while 5.0 - 7.5 mg/l makes the water completely undrinkable (Schneider, 1931). For this reason it is believed that copper is seldom a hazard to domestic supplies.

Copper is present in trace amounts in all living organisms. It is believed to be essential for nutrition.

The toxicity of copper to aquatic organisms varies significantly not only with the species, but also with the physical and chemical characteristics of the water (e.g., temperature, hardness, turbidity, and carbon dioxide content). Concentrations, toxic to a variety of aquatic organisms, may vary from 0.015 to 3.0 mg/l depending upon the water chemistry.

Copper acts synergistically with the sulfates of other metals such as zinc and cadmium to produce a potent toxic effect on fish (Anonymous, 1950; Doudoroff, 1952; and Tarzwell, 1958). Synergism also exists between copper and mercury (Corner and Sparrow, 1956).

Standards

Limits set for copper in water vary markedly. The following table summarizes agency recommendations.

CADMIUM (Cd)

Water Quality

The elemental form of cadmium is insoluble in water, although the chloride, nitrate, and sulfate of this metal are highly soluble. In the literature searched no "normal" level for freshwater was recorded. Mention was made of "normal" levels for seawater of <0.08 mg/l (FWPCA, 1968).

Cadmium salts may be found in wastes from electroplating plants, pigment works, textile printing, lead mines and certain chemical industries. Welsch and Lieber (1954) reported groundwater contamination by cadmium to the extent of 3.2 mg/l on Long Island, N.Y., as the result of an electroplating industry's waste discharge. High concentrations of cadmium have been reported in Missouri mine waters (Anonymous, 1955). One spring in the area had 1,000 mg/l of cadmium.

TABLE 2. Copper (Cu) Concentration (mg/l)

Copper Concentration	Organization & Date of Recommendation	Comment
0.2	USPHS, 1925	Mandatory maximum limit for drinking water.
3.0	USPHS, 1942	Recommended limit for drinking water (not mandatory).
3.0	USPHS, 1946	Recommended limit for drinking water (not mandatory).
3.0	State of Oklahoma, 1957	Limit for municipal water supply.
0.2	State of Oklahoma, 1957	Limit for agricultural water use.
1.0	State of Oklahoma, 1957	Limit for recreational waters.
1.0	W.H.O., 1958	Permissible limit for drinking water.
1.5	W.H.O., 1958	Excessive limit for drinking water.
3.0	W.H.O. European, 1961	Limit after 16 hours contact with new pipe, but distribution system should have <0.05 mg/l copper.
1.0	USPHS, 1962	Recommended limit for drinking water.
1.0	State of California, 1963	Threshold concentration in domestic supplies.
0.1	State of California, 1963	Threshold concentration in irrigation supplies.
0.02	State of California, 1963	Threshold concentration for freshwater fish and aquatic life.
0.05	State of California, 1963	Threshold concentration for seawater fish and aquatic life.
1.0	State of Texas, 1967	Recommended limit for inland and tidal waters.
	FWPCA, 1968	Water Quality Criteria for aquatic life. Maximum copper concentration at any time or place should not be greater than 1/10 the 96-hour TL_m

Copper Concentration	Organization & Date of Recommendation	Comment
	FWPCA, 1968 (Continued)	value, nor should any 24-hour average concentration exceed 1/30 of the 96-hour TL_m value.
1.0	State of Alaska (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
1.0	State of Connecticut (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
0.5	State of Florida (date unknown)	Maximum allowable limits for surface waters to be used for drinking water, shellfish, fish and wildlife, and industrial water supply.
1.0	State of Illinois (date unknown)	Maximum allowable for drinking water.
1.0	State of Maine (date unknown)	Maximum allowable for drinking water.
1.0	State of Michigan (date unknown)	Same As USPHS, 1962, Drinking Water Standards.
1.0	State of Minnesota (date unknown)	Maximum allowable limit for drinking water.
0.2	State of Minnesota (date unknown)	Maximum allowable limit for recreation water, fish propagation and wildlife.
1.0	State of Montana (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
1.0	State of Nevada (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
1.0	State of Rhode Island (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
1.0	State of Vermont (date unknown)	Same as USPHS, 1962, Drinking Water Standards.

Biotic Response

Cadmium is moderately toxic to all organisms and it is a cumulative poison in mammals. It tends to concentrate in the liver, kidneys, pancreas, and thyroid of humans and other mammals.

Common levels found in marine plants are approximately 0.4 mg/l, while in marine animals a range of 0.15 to 3 mg/l has been recorded (FWPCA, 1968).

Few studies have been made of the toxicity of cadmium in the aquatic environment. Medical reports are of little value because the adverse effects of human ingestion vary appreciably from person to person.

Aquatic organisms (i.e., *Daphnia magna*) are currently being exposed to cadmium and other toxic metals via bioassay techniques at EPA's Duluth, Minnesota, laboratories. Preliminary results indicate *Daphnia* are very sensitive to cadmium; the LC-50 (3 wk.) was 5 mg/l in Lake Superior water. Other unpublished data (Biesinger, Christensen, Shelhom, in press) reveal no effect to fathead minnows or bluegills exposed to 37 μg/l through a complete generation. The tests also indicate that following prolonged exposure there is a large accumulation of cadmium in fish (personal communication, J. I. Teasley).

Cadmium acts synergistically with zinc to increase toxicity. Hublou, Wood, and Jeffries (1954) found that cadmium concentrations of 0.03 mg/l in combination with 0.15 mg/l of zinc from galvanized screens caused mortality of salmon fry.

Standards

Because scant data are available as to the long-term adverse effects of cadmium on the environment, the standards are possibly excessively restrictive.

TABLE 3. Cadmium (Cd) Concentrations (mg/l)

Cadmium Concentration	Organization & Date of Recommendation	Comment
0.1	USSR, 1949	Maximum permissible concentration in domestic supplies of Russia.
0.0	State of Oklahoma, 1957	Suggested criteria for municipal, industrial, agricultural, recreation, fish and wildlife water use.
0.05	W.H.O. European, 1961	Maximum tolerance limit for drinking water.
0.01	USPHS, 1962	Maximum allowable limit for drinking water.
0.02	State of Texas, 1967	Maximum limit for inland and tidal waters.
	FWPCA	The concentration of cadmium must not exceed 1/30 of the 96-hour TL_m concentration at any time or place and the maximum 24-hour average concentration should not exceed 1/500 of the 96-hour TL_m concentration.
0.01	State of Alaska (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
0.01	State of Colorado (date unknown)	Maximum allowable limits for drinking water.
0.01	State of Connecticut (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
0.01	State of Illinois (date unknown)	Maximum allowable limit for drinking water.
0.05	State of Illinois (date unknown)	Maximum allowable limit for fish propagation and wildlife waters.
0.01	State of Indiana (date unknown)	Maximum allowable for drinking water.
0.01	State of Iowa (date unknown)	Maximum allowable for drinking water.

TABLE 3. Cadmium (Cd) Concentrations (mg/1) - Continued

Cadmium Concentration	Organization & Date of Recommendation	Comment
0.01	State of Maine (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
0.01	State of Michigan (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
0.01	State of Minnesota (date unknown)	Maximum allowable for drinking water.
0.01	State of Mississippi (date unknown)	Maximum allowable for drinking water.
0.01	State of Montana (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
0.01	State of Nevada (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
0.01	State of Ohio (date unknown)	Maximum allowable limit for drinking water.
0.01	State of Rhode Island (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
0.01	State of Vermont (date unknown)	Same as USPHS, 1962, Drinking Water Standards.

LEAD (Pb)

Water Quality

Some natural waters contain lead in solution, as much as 0.8 mg/l (Lambou and Lim, 1970b). These concentrations are most often found in mountain streams flowing through limestone and galena. Surface and groundwaters used for drinking supply in the U.S. often have a trace of lead but it seldom exceeds 0.04 mg/l (Ohio River Sanitation Commission, 1953).

The lead concentration in seawater is about 0.00003 mg/l. It is found in marine plants at a level of 8.4 mg/l. Residues in marine animals reach a concentration in the range of 0.5 mg/l. Lead is highest in calcareous tissue (FWPCA, 1968).

Higher concentrations than listed above are usually the result of pollution from mines or leaded gasolines.

Biotic Response

Lead tends to be deposited in bone as a cumulative poison. Sensitivity to lead poisoning differs with individuals as concentrations causing human sickness may vary from 0.042 to 1.0 mg/l (Mason, 1908).

Abundant bioassay data are available (see McKee and Wolf, 1963 p. 208). Lead has an antagonistic effect with calcium. In soft water, lead may be very toxic at concentrations of 0.1 mg/l (Doudoroff and Katz, 1953). In hard water these concentrations are not toxic. As a matter of fact, the Ohio River Valley Water Sanitation Commission (Anon., 1950) reported that calcium in a concentration of 50 mg/l completely destroyed the toxic effect of 1.0 mg/l of lead.

Standards

In recent years the USPHS standard for lead in drinking water has been lowered. The major reason for this lowering of limits is that

TABLE 4. Lead (Pb) Concentration (mg/l)

Lead Concentration	Organization & Date of Recommendation	Comment
0.1	USPHS, 1925	Maximum permissible concentration in drinking water.
0.3	Germany, 1933	Temporary concentration in drinking water that had been in pipes for 24 hours.
0.1	USPHS, 1942	Maximum permissible concentration in drinking water.
0.1	USPHS, 1946	Maximum permissible concentration in drinking water.
0.02	Uruguay, 1951	Maximum recommended limit in potable water.
0.3	Netherlands, 1953	Temporary concentration in drinking water that had been in pipes for 24 hours.
1.0	Mersey and Severn River Boards in England (date unknown)	Working standards for all heavy metals in certain English streams.
0.1	W.H.O. International, 1958	Maximum allowable limits for lead in drinking water.
0.1	International Water Supply Assoc. (USA, Great Britain, France, and Netherlands), 1958	Maximum allowable limits for lead in drinking water.
0.1	W.H.O. European, 1961	Maximum tolerance limit for drinking water.
0.05	USPHS, 1962	Maximum allowable limit for drinking water.
0.1	State of California, 1963	Maximum limit for surface waters used by fish or to be processed for human consumption.
0.1	State of Texas, 1967	Maximum limit for inland waters.
0.5	State of Texas, 1967	Maximum limit for tidal waters.

Lead Concentration	Organization & Date of Recommendation	Comment
0.05	FWQA, 1970	Physiologically safe in water for lifetime.
2-4	FWQA, 1970	Physiologically safe in water for period of a few weeks (borderline health hazard thereafter).
8-10	FWQA, 1970	Toxic in water with exposure of several weeks.
>15	FWQA, 1970	Lethal, unknown concentration, probably more than 15 mg/l for a period of several weeks.
0.05	State of Alaska (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
0.05	State of Colorado (date unknown)	Maximum allowable limit for drinking water.
0.05	State of Connecticut (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
0.05	State of Florida (date unknown)	Maximum allowable limit for drinking water, industrial supply, agriculture, fish propagation and wildlife, and recreation.
0.05	State of Illinois (date unknown)	Maximum allowable limit for drinking water.
0.1	State of Illinois (date unknown)	Maximum allowable limit for fish propagation and wildlife waters.
0.05	State of Indiana (date unknown)	Maximum allowable limit for drinking water.
0.05	State of Iowa (date unknown)	Maximum allowable limit for drinking water.
0.05	State of Maine (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
0.05	State of Minnesota (date unknown)	Maximum allowable limit for drinking water.

Lead Concentration	Organization & Date of Recommendation	Comment
0.05	State of Mississippi (date unknown)	Maximum allowable limit for drinking water.
0.05	State of Nevada (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
0.05	State of Ohio (date unknown)	Maximum allowable limit for drinking water.
0.05	State of Rhode Island (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
0.05	State of Vermont (date unknown)	Same as USPHS, 1962, Drinking Water Standards.

control causes little undue hardship on water purveyors, and total cumulative ingestion by the consumer is reduced.

ZINC (Zn)

Water Quality

Some zinc salts (e.g., zinc chloride and zinc sulfate) are highly soluble in water. These salts are often found in industrial wastewater from galvanizing industries, and manufacturers of paint pigments, cosmetics, pharmaceutics, dyes, insecticides, and numerous other products. In zinc-mining areas, this metal has been found in natural waters in concentrations as high as 50 mg/l (American Water Works Assoc., 1950).

In most freshwater (surface and ground), zinc is present only in trace amounts. Jacobs (1953) presented some evidence that zinc ions are absorbed strongly and permanently on silt, with the resultant inactivation of the metal.

In seawater, the normal zinc concentration is about 0.01 mg/l. Marine plants may contain up to 150 mg/l of zinc, while marine animals contain ranges of 6 to 1,500 mg/l.

High concentrations of zinc in domestic water are undesirable from an aesthetic standpoint as well as from a health hazard standpoint. (Note: health hazards are discussed later.) At a concentration of 30 mg/l, zinc gives water a milky appearance (Kehoe, Cholak, Largent, 1944). Concentrations as low as 5.0 mg/l cause a greasy film on boiling of the water (Howard, 1923).

The soluble salts of zinc impart an unpleasant, astringent taste to water and can be detected as low as 4.3 mg/l (Cohen, Kamphake, Harris, and Woodward, 1960).

Biotic Response

Zinc has no known adverse physiological effects upon man except at very high concentrations (i.e., 675-2,280 mg/l causes vomiting). In fact, zinc is an essential and beneficial element in human nutrition (Rothstein, 1953). Normal uptake by humans is 10-15 mg/day (Browning, 1961).

Zinc exhibits its greatest toxicity toward fish and aquatic organisms. In soft water, concentrations of zinc ranging from 0.1 to 1.0 mg/l have been reported to be lethal, but calcium is antagonistic toward such toxicity.

Fish sensitivity to zinc varies with species, age and condition of the fish, as well as the physical and chemical characteristics of the water. Bioassay results are listed in detail by McKee and Wolf, 1963, p. 295).

There is some controversy as to a synergistic effect between zinc and copper. Doudoroff and Katz (1953) believe a synergistic effect exists while the Water Pollution Research Board of England (1960) disagrees. The key to this disagreement appears to be the hardness of the water, but more study will be required before a definite statement can be made.

Standards

Zinc "taste tests" have been partly instrumental in changing the standards for potable supply. This is one reason for the range in limits listed in Table 5.

TABLE 5. Zinc (Zn) Concentration (mg/1)

Zinc Concentration	Organization & Date of Recommendation	Comment
5.0	USPHS, 1925	Maximum permissible concentration in drinking water.
15.0	USPHS, 1942	Recommended limited concentration in drinking water.
15.0	USPHS, 1946	Recommended limited concentration in drinking water.
1.0	Mersey and Severn River Boards in England, 1953	Working standards in English streams for all heavy metals in combination with zinc.
5.0	W.H.O. International, 1958	Permissible limit in drinking water.
15.0	W.H.O. International, 1958	Excessive limit in drinking water.
5.0	W.H.O. European, 1961	Recommended limit for drinking water.
5.0	USPHS, 1962	Recommended limit for drinking water.
5.0	State of Texas, 1967	Maximum limit for inland and tidal waters.
5.0	State of Alaska (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
5.0	State of Connecticut (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
1.0	State of Florida (date unknown)	Maximum allowable for drinking water, industrial supply, agriculture, fish and wildlife, and recreation.
5.0	State of Illinois (date unknown)	Maximum allowable for drinking water.
1.0	State of Illinois (date unknown)	Maximum allowable for fish and wildlife waters.

Zinc Concentration	Organization & Date of Recommendation	Comment
5.0	State of Maine (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
5.0	State of Michigan (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
5.0	State of Minnesota (date unknown)	Maximum allowable in drinking water.
5.0	State of Montana (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
5.0	State of Nevada (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
5.0	State of Rhode Island (date unknown)	Same as USPHS, 1962, Drinking Water Standards.
5.0	State of Vermont (date unknown)	Same as USPHS, 1962, Drinking Water Standards.

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