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**A REVIEW OF CURRENT INFORMATION ON SOME
ECOLOGICAL AND HEALTH RELATED ASPECTS OF THE
RELEASE OF TRACE METALS INTO THE ENVIRONMENT
ASSOCIATED WITH THE COMBUSTION OF COAL**

By
Merrill Heit

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Health and Safety Laboratory
U.S. Energy Research and Development Administration
New York, New York 10014

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Health and Safety Laboratory
Energy Research and Development Administration
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ABSTRACT

A review of recent information on the environmental levels, ecological effects and health effects of thirty five elements which may be released into the environment by the combustion of coal is presented. Elements discussed include: Ag, Al, As, B, Ba, Be, Bi, Cd, Co, Cr, Cu, F, Fe, Ga, Ge, Hf, Hg, In, Mn, Mo, Ni, Pb, Rb, Sb, Sc, Se, Sn, Sr, Te, Ti, Tl, U, V, W and Zn.

Fourteen of these elements are found to be potentially harmful to organisms from various ecosystems either through direct contact or secondarily through incorporation in food chains. Of these, the trace elements found to be potentially harmful to man and usually other biota include: As, Be, Cd, Cr, Hg, Ni, Pb, Se, Sn and Tl. Those elements which are primarily deleterious to organisms other than man include: Ag, Cu, F and Zn.

Another six elements Ba, Bi, Co, Ga, Mn and Te remain questionable as to whether they are of environmental concern. Vanadium is important as an indicator of the combustion of fossil fuels.

INTRODUCTION

The Middle East oil embargo of 1973-74 has resulted in the United States initiating programs which are designed to lead to energy independence. These programs will cause:

- a. an increase in the use of coal combustion for electric power generation, and
- b. an increase in the production of fuels and chemicals produced synthetically from coal.

Materials identified to date in the literature as possibly being released into the environment during coal combustion or gasification are listed in Table 1.⁽¹⁻¹⁰⁾ All of these substances eventually will enter aquatic and terrestrial systems and may move through these systems to man. Research to date on the effects of these pollutants on ecosystems, levels in the environment, and their transport to man has been scattered and often times is completely lacking.

This report is a review of the literature on one class of these pollutants, trace elements, their occurrence in the environment and their potential toxicity to man.

GENERAL OVERVIEW OF THE LITERATURE

Considerable attention has been given to the problems associated with the release of trace metals into the environment. However, most of the studies that have been conducted in the past have dealt with acute effects of particular trace metals on laboratory animals and human health, rather than their levels in the environment and their long term chronic effects. A summary of the health effects of trace metals on humans and laboratory animals is presented in Table 2.⁽¹¹⁻¹⁶⁾

Most of the research that has been conducted on the levels of trace metals in the environment and their ecological effects have been investigations of mercury, and to a lesser extent, cadmium and lead. Compared to the number of studies cited in the literature for these substances, the information available on other trace metals is spotty at best and almost non-existent in

most cases.

In general, a wide range of trace metals have been found in coal (see Table 3).^(1-3,6-10,17) Studies have shown that the trace element composition of coal varies greatly even within a given locality. However, most trace elements in coal occur in concentrations which approximate the earth's continental crustal material.⁽¹⁰⁾

The anthropogenic contribution of trace elements to the environment from the combustion of fossil fuels has been estimated to be significant for many of these elements^(3,7,8,18,19) (see Tables 4 and 5). In one study,⁽¹⁹⁾ it was shown that the elemental additions due to coal combustion were never less than 1.5% of their mobilization by weathering and that coal combustion also introduced As, Co, Cu, Fe, Hg, Mo, Ni, Pb, Sc, U, V and Zn into the environment at rates comparable to that of weathering. Researchers at Lawrence Livermore Laboratory⁽²⁾ have estimated that over one billion tons/year of coal may be burned in 1990. They predict that this may result in yearly releases into the environment of 28×10^6 lbs. arsenic, 2×10^6 lbs. cadmium, 20×10^6 lbs. lead, 30×10^6 lbs. nickel and 0.4×10^6 lbs. of mercury.

The order of volatility of trace elements depends upon their different chemical states. When volatilized by a DC arc, the order of volatility of Ag, As, Bi, Co, Cu, Ga, Ge, Hg, In, Rb, Sb, Sn, Tl and Zn was found to be as follows:⁽³⁾

1. As volatile oxides, sulfates, carbonates, silicates and phosphates: As, Hg > Cd, Pb, Bi, Tl > In, Ag, Zn > Cu, Ga > Sn > Rb.
2. In the elemental state: Hg > As > Cd > Zn, Sb \approx Bi > Tl > Mn > Ag, Sn, Cu > In, Ga, Ge.
3. As sulfides: As, Hg > Sn, Ge \approx Cd > Sb, Pb \approx Bi > Zn, Tl > In, Cu > Co, Ni, Mn, Ag.

Thus, one might expect a preferential release of arsenic, cadmium, mercury, lead, and thallium to the atmosphere. Recent mass balance and particulate studies have in fact shown that many of the elements are, as expected, concentrated in the ash (Ag, Al, B, Ba, Co, Cr, Cu, Fe, Ge, Mn, Rb, Sc, Sn, Ti, Th, W, Zn), while a few percent of these substances are released into the environment as particulates or gases. Other elements are volatilized to the extent of 50% or more (As, Cd, Hg, Pb, Sb, Se, Te, Tl), whereas

still others are volatilized to a somewhat lesser extent (Be, Mo, Ni, V).^(8,10,20-24)

The trace element content and species in vapors and particulate matter produced by the combustion of fossil fuels is mainly unknown.^(23,25) Arsenic has been shown to be emitted in sufficient quantities to modify the aerosol content downwind of coal fired plants. Similar results have been found for mercury and selenium. The metals As, Tl, Cd, Se, Pb and Sb are concentrated in fly ash particles of respirable size. These particles, 1-2 microns in diameter, contain between 3 and 18 times more of the above toxic metals than fly ash particles greater than 40 microns in diameter. These six metals are concentrated on the surface of the fly ash due to their vaporization and recondensation on the particle surface.^(26,27)

The elements Ag, Cd, Co, Cr, Cu, Fe, Hg, Ni, Ti and Zn have been found to be enriched in soils around a coal fired power plant whereas, Cd, Fe, Ni and Zn were found to be enriched in plant material. The enhanced metal content in the soil was found to be in general agreement with the wind roses for the area and metal content of the coal except for mercury which was only slightly enriched.⁽²⁸⁾ It should be noted that all of these substances, the volatile, semi-volatile and the refractory material in the ash, will all be released into the environment to some extent.

Summaries of the trace metal content of some crustal materials, water, foods and biota are presented in Tables 6-10.^(2,18,29-34)

In general, from the information available on their toxicity to humans, released amounts and ecological effects, the trace elements released from coal which are of greatest environmental concern in at least one of their chemical forms are: arsenic, beryllium, cadmium, copper, chromium, fluorine, lead, mercury, nickel, selenium, silver, thallium, tin and zinc. While little information is available on the occurrence of antimony, barium, bismuth, cobalt, gallium and tellurium in the environment, there are some reports of at least their potential toxicity and thus they remain as possible environmental hazards (see Table 11).⁽³⁵⁾ Vanadium, although not toxic, remains important as an indicator of the combustion of fossil fuels.

The following is a general survey of the background levels, and the health and ecological effects of some of the trace elements found in coal. Those elements which are toxic to mammals or potentially destructive to aquatic and terrestrial ecosystems are emphasized. The elements are presented in alphabetical order by symbol.

1. Ag (Silver)

Silver is toxic to marine organisms. It has been found to be concentrated from sea water by factors ranging from 80 for marine algae up to 1,000 for marine mammals. Concentrations of silver as low as 2 $\mu\text{g}/\ell$ have been found to delay development and cause deformations in sea urchins.⁽³⁶⁾ Silver may also cause significant respiratory depression in marine teleosts after exposures to concentrations as low as 0.12 $\mu\text{g}/\text{g}$.⁽³⁷⁾

Silver does not occur normally in animal or human tissues. The major effects of excessive exposure to silver is a local or generalized impregnation of the tissues known as argyria. It is not known to harm individuals in any way other than its unsightly appearance. Silver can be absorbed from the lungs and gastrointestinal tract. Excretion of ingested silver is primarily via the gastrointestinal tract.⁽¹¹⁾

2. Al (Aluminum)

Aluminum is toxic to plants in acid soils, however, at pH values between 5.5 and 8.0 soils precipitate soluble aluminum so as to eliminate its toxicity.⁽³⁸⁾

Only massive oral doses of aluminum are reported to be toxic to mammals.⁽¹¹⁾

3. As (Arsenic)

Arsenic is ubiquitous in the environment, occurring in various forms. Trivalent arsenic compounds (arsenite) are, in general, more toxic than pentavalent compounds (arsenate). In nature, the arsenate compounds are more prevalent than the arsenite compounds. Arsenic may also be methylated by micro-organisms.

Arsenic occurs primarily in the pentavalent form in the soil.⁽³⁸⁾ The formation of arsenic compounds is affected by acidity and the Fe, Al, Ca, P, and humus content of the soil. Soils with high reactive aluminum levels have been found to be less phytotoxic even after heavy applications of arsenic.⁽³⁹⁾ Arsenic toxicity has been observed in plants growing on soils treated with arsenical pesticides, herbicides and defoliants. These plants were found to contain relatively low levels of arsenic probably due to its action as a metabolic inhibitor.⁽⁴⁰⁾ When present in soils, toxic amounts of arsenic arrest the germination of seeds and reduce the viability of seedlings. In

addition, the rate of nitrification in the presence of arsenic in soils is decreased.⁽³⁹⁾

Arsenic is a cumulative poison with long term chronic effects on both aquatic organisms and on mammalian species. There is some evidence that arsenic is concentrated in aquatic food chains, often reaching concentrations in excess of proposed EPA standards.⁽⁴¹⁾ There is little information on the accumulation of arsenic in fresh water organisms. Some species of freshwater fish have been reported to concentrate arsenic by a factor of 20-130 above the concentration in water.⁽⁴²⁾ The fresh water invertebrates Daphnia sp. and crayfishes have also been reported to concentrate arsenic.⁽⁴³⁾

Arsenic is accumulated by many marine fauna. Marine algae have also been reported to concentrate arsenic.⁽⁴⁰⁾ Arsenic also tends to be accumulated by oysters and other marine shellfish where concentrations of up to 100 µg/g have been reported.⁽⁴⁴⁾

The toxicity of arsenic to humans depends upon its chemical form. Organic arsenic compounds are considerably more toxic than the inorganic forms which occur in living tissues or are used as feed additives. Differences in toxicities of various forms are clearly related to their rates of excretion, the least toxic being the most rapidly eliminated.⁽⁴⁵⁾ Arsenic has been shown to accumulate in the body faster than it is excreted. It can build to toxic proportions from small amounts absorbed from periodic exposure or dietary contamination.⁽⁴⁶⁾ Arsenate is excreted rapidly from the kidneys and probably does not accumulate in humans. Arsenites accumulate in the liver, muscle, hair, nails and skin. Intake of arsenic by man has been implicated in skin and respiratory cancer.⁽¹¹⁾

Most arsenic is ingested by humans in fish, meat and poultry (56%), dairy products (23%), grain and cereal (14%), and potatoes (6%).⁽⁴⁷⁾

4. B (Boron)

Boron occurs regularly in natural water supplies and in plant and animal tissues. It is an essential nutrient to plants, but not to animals. While essential for growth at higher concentrations, boron is very toxic to many terrestrial plants and produces adverse effects at concentrations exceeding 1.0 mg/l of water.⁽³⁶⁾ Available data on toxicity of boron to aquatic organisms are mostly from fresh water. Since the toxicity of boron is slightly lower in hard water than in distilled water, it is anticipated that

boric acid and borates would be less toxic to marine aquatic life than to fresh water organisms.⁽³⁶⁾ The effects of boron on marine vegetation are unknown.⁽³⁶⁾

Boron has a low order of toxicity to livestock with no evidence of accumulation in mammalian tissues.⁽³⁶⁾ However, in lambs, gastrointestinal and pulmonary disorders have been reported as a result of grazing on vegetation growing in areas of high boron soil content.⁽¹¹⁾ The ingestion of 16-20 g of boric acid per day for 40 days produced no ill effects in dairy cows.⁽³⁶⁾

In humans, practically all of the boron is absorbed from food and excreted via the kidneys. It has been reported that concentrations as high as 30 mg/l of water are not harmful to man.⁽⁴⁸⁾

5. Ba (Barium)

Barium is relatively common in nature and occurs in plant and animal tissues.⁽¹¹⁾ Plants have been shown to accumulate barium from soil.⁽¹¹⁾

All water and acid soluble barium compounds are reported to be poisonous. However, the sulfate and carbonate present in sea water precipitate barium and thus tends to mitigate its effects on marine life.⁽³⁶⁾ Some concentration factors from sea water for barium have been reported as 17,000 for phytoplankton, 900 for zooplankton, and 8 for fish muscle.^(36,44) An accumulation of radioactive barium in the internal organs, gills and scales of fish from the northwest Pacific has also been reported.^(36,49)

Of the barium which is ingested, only a small amount is retained in mammals for periods greater than 24 hours. Very low concentrations have been found in the mammalian kidney, spleen, skeletal muscle, heart, brain, liver, and skeleton.⁽¹¹⁾ The toxicity of barium to mammals depends upon the chemical species. Insoluble forms of barium, such as barium sulfate, are not toxic whereas soluble barium compounds are highly toxic. The lethal dose to humans is considered to be between 0.8 and 0.9 grams of barium chloride. At present, there are no studies revealing how much barium is tolerable in drinking water nor have any studies been made of the long term effects of the consumption of barium.⁽³⁶⁾

6. Be (Beryllium)

The addition of beryllium to soil has been shown to have some effects on plant growth. For example, some varieties of citrus fruit seedlings show toxic effects at concentrations of

2.5 - 5 $\mu\text{g}/\ell$ beryllium.⁽⁵⁰⁾ In addition, beryllium has been shown to inhibit photosynthesis and growth in some crop plants.⁽⁵¹⁻⁵³⁾ However, it is unknown if the same effect occurs in marine flora where it has been reported to be concentrated by a factor of 1000.^(36,54)

Beryllium is not well absorbed when given to humans by any route. After inhalation, beryllium is retained in the lungs and is mobilized slowly. The beryllium which is absorbed by the body is mostly excreted in the urine.⁽¹¹⁾ In humans, beryllium has been shown to produce many effects depending upon the dose and duration of exposure. The most extensive changes usually occur in the lungs.⁽¹¹⁾ At present, it is not clear if exposure to beryllium compounds is associated with an increase in the incidence of carcinomas in humans.⁽¹²⁾ The salts of beryllium are not highly toxic for intake by ingestion since laboratory rats survived for two years on a diet containing beryllium at a concentration of 18 mg/kg body weight daily.⁽³⁶⁾

7. Bi (Bismuth)

Little is known of the effects of bismuth on either terrestrial or aquatic systems. Concentrations of 0.04 to 0.3 mg/ ℓ have been reported for marine animals, indicating concentration factors up to 10,000.^(36,54) Bismuth has a fairly low level of toxicity to mammals. It causes kidney and liver damage only when ingested in large doses.⁽⁵⁵⁾

8. Cd (Cadmium)

Cadmium is stated to be "an extremely dangerous cumulative toxicant causing insidious, progressive chronic poisoning in mammals, fish and probably other animals, because the metal is excreted at a very low rate."⁽³⁶⁾

Cadmium is always found in association with zinc in the earth's crust.⁽⁵⁶⁾ Cadmium does not degrade in the environment but rather accumulates in soils and sediments where it may enter various food chains.⁽¹²⁾ When present in soils, cadmium is apparently readily taken up by a great number of plant species especially the grasses and grains (e.g., wheat, corn, rice, oats and millet).⁽⁵⁷⁻⁵⁸⁾ Cadmium is also found in peas, beets, lettuce and radishes. The concentration of cadmium reported to be present in an average background soil is 0.55 $\mu\text{g}/\text{g}$, with plants growing in this soil containing 0.12 $\mu\text{g}/\text{g}$ Cd. Similar soils present around a coal fired power plant were found to have 1.46 $\mu\text{g}/\text{g}$ Cd and the plants growing in this soil had an average of 0.35 $\mu\text{g}/\text{g}$

Cd.⁽⁹⁾ Yields of some crop plants may be reduced up to 25% by the addition of cadmium to nutrient solutions at concentrations greater than 100 µg/l.⁽³⁶⁾ The mechanisms by which cadmium is taken up by plants is still largely unknown.⁽⁵⁹⁾ In addition, there is a lack of information on the behavior of cadmium in terrestrial ecosystems and its transport through food chains.

In fresh water systems, floating aquatic plants have been found to accumulate cadmium from concentrations as low as 0.01 µg/g. Although this results in inhibited growth, the concentrations of the metal which accumulated in the leaves and fronds was up to 82 µg/g or a concentration factor of 8200.⁽⁶⁰⁾

Little data is available on the cadmium content of marine and freshwater fish, but it does concentrate in the liver.^(61,62) Of these few aquatic organisms studied for cadmium uptake, mollusks received most of the attention.^(63,64) The mollusks accumulate their cadmium in calcareous tissues and in the vicera. Concentration factors of 1000 for cadmium have been reported in fish muscle, as have concentration factors of 3,000 in marine plants and up to 30,000 in some marine animals.⁽³⁶⁾ Cadmium is also known to have marked acute and chronic effects on aquatic organisms. The eggs and larvae of fish are apparently more sensitive than adult fish to poisoning by cadmium, while crustaceans appear to be more sensitive than fish eggs and larvae.⁽⁵⁶⁾ Cadmium is particularly toxic to gill bearing marine and freshwater crustaceans and may induce ultra-structural changes in the gills.⁽⁶⁵⁾

In mammals, approximately 6 to 10% of the ingested cadmium is absorbed and transported through the body by red blood cells. Cadmium collects in the kidney, liver, pancreas and blood vessels. Some cadmium is absorbed from the lungs following inhalation. The amount of cadmium uptake from material in the lungs depends on the concentration, particle size, solubility of the particulate matter and physiological considerations. However, under normal conditions, inhalation does not contribute significantly to intake. Most cadmium salts have a short retention time in the lungs.^(11,66)

The kidney has been the initial target organ of retained cadmium. Some symptoms of cadmium poisoning can be prevented by the presence of zinc, selenium, cobalt, estrogens, and cysteine.⁽¹¹⁾ Most cadmium enters the human diet from grains and cereals (23%), fruits (18%), potatoes (18%), beverages (13%), dairy products (8%), and meat, fish and poultry (5%).⁽⁴⁷⁾

Cadmium may enter the body via the gastrointestinal tract from ingestion of fish from polluted waters. When ingested at very high concentrations, it may cause itai itai (ouch ouch) disease as reported in Toyama Bay, Japan.⁽⁶⁷⁾ Cadmium, as has been reported for mercury, may form organic compounds in aquatic systems which may be highly toxic or lead to mutagenic or teratogenic effects when ingested.⁽³⁶⁾

9. Co (Cobalt)

Cobalt has been reported to increase in concentration in the soil around a coal fired power plant from 2.3 $\mu\text{g/g}$ in background soil to 4.6 $\mu\text{g/g}$ in enriched soils near the plant.⁽²⁸⁾

Cobalt is an essential element for both plants and animals. In mammals it is required for activation of vitamin B₁₂.⁽¹¹⁾ The difference between nutritional requirements and toxic dosage in plants may be very small. A concentration of 0.1 mg/l of cobalt in nutrient solutions in irrigation waters is near the threshold toxicity level of plants, whereas a concentration of 0.05 mg/l appears to be satisfactory for continuous application on all soils.⁽⁶⁸⁾ For wildlife and domestic animals, such as sheep and cattle, a wide margin of safety (a factor of 100) exists between the required and toxic levels.⁽³⁶⁾ However, the slow accumulation of cobalt at a concentration of 1 $\mu\text{g/g}$, over a period of time as short as a month, results in cardiomyopathy (similar symptoms to congestive heart failure) in laboratory organisms.⁽¹¹⁾ In man, cobalt salts are well absorbed by the small intestine. However, significant retention of cobalt by humans does not occur. Approximately 80% of the ingested cobalt is excreted in urine, and 15% is removed in the feces.⁽¹¹⁾

10. Cr (Chromium)

The concentration of chromium in soils varies greatly, however, the soil chemistry of chromium is largely unknown.⁽²⁾ In some agricultural crops, high levels of chromium can cause reduced growth or death of the crops, whereas adverse effects of low concentrations of chromium on corn, tobacco and sugar beets have also been documented.⁽⁶⁹⁾ The oxides of chromium in the soil are very insoluble and generally unavailable to plants.

As with other metals, the toxicity of chromium salts for aquatic life varies with the species, temperature, pH, valence, and the presence of synergistic and antagonistic substances.⁽³⁶⁾ Chromium toxicity is especially sensitive to water hardness.⁽³²⁾ Fish are relatively tolerant to chromium salts, but lower forms

of aquatic life are extremely sensitive. Chromium also inhibits the growth of algae. The reported lethal limits of hexavalent chromium for fish are 17 and 18 mg/l as compared to 0.05 mg/l for macroinvertebrates and 0.032 to 6.4 mg/l for algae.⁽³⁶⁾

Chromium is only biologically important in the tri- and hexavalent states. In mammals, there is a conversion of hexavalent to trivalent chromium. Trivalent chromium is postulated to be an essential element to mammals.⁽¹¹⁾ Even in its most soluble forms, chromium is not absorbed by mammals and is largely excreted in the feces.^(32,36) Also, it does not appear to concentrate in any particular mammalian tissues or to increase in these tissues with age.^(36,70)

Most human exposure to chromium occurs via intake of food and water. However, the presence of chromium in these substances has not produced any significant adverse effects in either man or experimental animals.⁽¹¹⁾ It should be noted that chromium passes through the placenta and enters the fetus, where it is selectively concentrated in the lung tissue. There is also the possibility of occupationally induced lung cancer due to the inhalation of hexavalent chromium.^(11,69)

11. Cu (Copper)

Copper is an essential element for most organisms. However, it can be strongly toxic to plants and aquatic organisms even at very low concentrations when present in its ionic form.^(71,72)

In general, copper concentrations less than 1 mg/l have been reported to be toxic to many kinds of fish, crustaceans, molluscs, insects, phytoplankton and zoo plankton.⁽³⁶⁾ The toxicity of copper varies between organisms. For example, diatoms, dinoflagellates and blue green algae are reported to be more sensitive than green algae to poisoning by Copper.⁽⁷¹⁾ Thus the enrichment of copper to an aquatic ecosystem would be expected to result in a reduction in primary productivity and the standing crop of many species of phytoplankton. The toxicity of copper to aquatic organisms is also affected by the physical and chemical characteristics of the water including temperature, hardness, turbidity, and carbon dioxide content. In hard water, the toxicity of copper salts is reduced by the precipitation of copper carbonate or other insoluble compounds.⁽³²⁾ Also, the sulfates of copper and zinc, and of copper and cadmium, are synergistic in their toxic effect on fish.⁽³⁶⁾ Copper is accumulated by many marine organisms, with concentration factors of 30,000 reported in phytoplankton,

5,000 in the non-calcareous tissues of molluscs and 1,000 in fish muscle. It is also concentrated in many aquatic invertebrates in which the copper is attached to their blood protein hemocyanin which serves as an oxygen carrier. ^(32,36,44)

Even when man is exposed to excessive concentrations of copper, chronic symptoms do not result. ⁽¹¹⁾ For humans, the only limiting factor of copper in domestic water supplies is taste. ⁽³⁶⁾

12. F (Fluorine)

Most studies of fluorine in the environment have been on its effects on food crops. It has been shown that airborne fluoride can damage either the foliage or the fruit of a wide range of plants. Citrus trees, apricot, cherry, plums, grapes, Douglas fir and many species of pine, corn, sorghum, and ornamental flowers, in particular, are extremely susceptible to fluoride damage. ⁽⁷³⁾

As a result of fluoride pollution and its entry into food chains by accumulation in forage crops, extensive damage to grazing livestock has occurred. Some plant varieties have been found to build up fluoride concentrations in their tissue to levels that are millions of times that found in the surrounding air. ⁽⁷³⁾

In contrast to terrestrial studies, data from field studies on bioaccumulation of fluoride in aquatic organisms are virtually non-existent. However, it is known that fluoride is taken up by some aquatic plants and is stored in the skeletons of fish. ⁽⁷⁴⁾

In vertebrates, fluoride is stored primarily in the skeletal tissue. Data from field studies on the levels and bioaccumulation of fluoride show that a level of 2.0 mg/l in livestock drinking water may result in some tooth mottling. This concentration is not excessive from the standpoint of animal health or the deposition of fluoride in meat, milk or eggs. Chronic fluoride poisoning of livestock has been observed when water contained 10 to 15 mg/l of fluoride. ⁽⁷⁵⁾ Concentrations of 30 to 50 mg/l of fluoride in the total ration of dairy cows is considered by the EPA to be the upper safe limit. ⁽³⁶⁾ Fluoride is transferred only to a very small extent into the milk and to a somewhat greater extent into eggs. ⁽³⁶⁾ However, fluoride uptake in ruminants can lead to prenatal skeletal defects. The presence of aluminum may mitigate the effect of fluorosis and it should be noted that aluminum comprises a fairly large portion of coal ash.

Fluoride may be transformed by some organisms in the natural environment into far more toxic organic fluorides. If this transformation occurs to any significant degree, it could have profound ecological effects.⁽⁷⁴⁾

13. Fe (Iron)

Iron is widely distributed in the environment with animal tissues usually having higher concentrations than plants. In mammals, iron is an essential element needed for the formation of hemoglobin and myoglobin. Because iron is homeostatically controlled, it is not toxic to man.⁽¹¹⁾ The addition of soluble iron salts in irrigation water may lead to increasing soil acidification.⁽³⁶⁾

14. Ga (Gallium)

Little is known of the toxicity of gallium to either plants or animals. There are no reported adverse effects of gallium in humans following industrial exposure. Gallium is not readily absorbed by mammals from the oral route.⁽¹¹⁾

15. Ge (Germanium)

The toxicity of germanium and its compounds is low to mammals even when present at very high levels. Inhalation exposure of rats to germanium and germanium oxide results in rapid clearance from their bodies.⁽¹¹⁾

16. Hf (Hafnium)

There are no reports of human toxicity due to hafnium.⁽¹¹⁾

17. Hg (Mercury)

Mercury is a particularly dangerous toxicant due to its volatility and transformation by bacterial action into an alkylated form.⁽⁷⁸⁾

The mercury content in soils of the United States ranges from 10 to 500 ng/g and averages 10 ng/g.⁽²⁾ Mercury tends to be retained in the surface layers of the soil due to adsorption by organic and inorganic materials and the low solubilities of mercury salts (phosphates, carbonate, sulfide).⁽²⁾ Mercury has been reported to increase in concentration in the soils around a coal fired power plant from 7.9 ng/g in background soils to 4.6 µg/g in enriched soils near the installation.⁽²⁸⁾

In most plants, mercury concentrations range from 10 to 200 ng/g (15 ng/g average), but plants growing near mercury deposits can contain 500 to 3,500 ng/g mercury. Translocation of mercury occurs in many plant tissues, including leaves, fruit and tubers. Toxicity of mercury to terrestrial plants apparently depends more on chemical form than on its concentration. There are few studies available on the toxicity of mercury to specific plants.⁽⁷⁷⁾

The occurrence of mercury is recognized as nearly ubiquitous in aquatic ecosystems. Most of the mercury in fish is in the methyl form.⁽⁷⁸⁾ In addition, numerous laboratory studies have demonstrated the toxicity of various mercury compounds to birds. Highest body burdens occur in fish-eating birds, as compared to insect-eating birds.⁽⁷⁹⁾ Presently, little is known about the overall effects of mercury on ecosystems. However, mercury is known to cause alteration of the behavior of various aquatic organisms.⁽⁸⁰⁻⁸²⁾

Concentrations of mercury in surface waters have usually been found to be far less than 5 $\mu\text{g}/\ell$. Natural methylation of bottom sediment mercury in areas bordering mercury deposits results in a continuous presence of the element in solution.⁽⁸³⁾ Mercury is actively taken up by lower orders of biota in freshwater aquatic ecosystems. More than 75% of all the methylmercury present in these lower orders is taken up directly from the water. Higher orders of aquatic biota, such as predatory fish, take up as much as 60% of their methylmercury directly from the water. At each higher trophic level, the concentration of methylmercury has been reported to increase due to binding in the muscle tissue.⁽⁸⁴⁾ The behavior of mercury in the marine environment is not completely understood. However, organo-mercurials are concentrated by marine organisms to a greater extent than are inorganic mercurials.^(40,85)

It is stated that all of the organic forms of mercury (alkoxy, alkyl, and aryl) are toxic, but the alkyl form is the most toxic to man. The accumulation and retention of these mercurials in the nervous system, the ease of their transmittal across the placenta, and their effect on developing tissue make them particularly dangerous to man.⁽⁸³⁾

Exposure to mercury vapor results in absorption by the lungs, with some secondary amounts taken in by the skin. Absorption of elemental mercury after oral ingestion is minimal compared to the uptake of methylmercury which is quickly absorbed through the skin, lungs and gastrointestinal tract. Methylmercury tends to accumulate in the kidney, brain and blood. In addition, methyl-

mercury may pass through the placental wall into the fetus, concentrating in the brain tissue.⁽¹¹⁾

Recently, it has been shown that the presence of selenium can decrease the toxicity of methylmercury in birds and rats.⁽⁸⁶⁾ The presence of selenium may also result in a decreased toxicity of methylmercury in fish such as tuna, which contains high levels of selenium.⁽⁸⁷⁾

18. In (Indium)

Indium is poorly absorbed from the gastrointestinal tract and is excreted in the urine and feces. In man, no industrial injury has been reported from the use of indium, nor has absorption of indium occurred from the use of indium-plated silver utensils.⁽¹¹⁾

19. Mn (Manganese)

Manganese is toxic at very low concentrations to many crop plants. However, its phytotoxicity is dependent upon acidic soil conditions.⁽³⁸⁾

Manganese primarily effects lower trophic levels of aquatic organisms. It has been shown to decrease growth and reproduction in some species of plankton, and cause increases in growth and reproduction in others.⁽⁸³⁾

Manganese is an essential element for mammals, being required as a cofactor for a number of enzymes. It is present in all living organisms and is absorbed from food via the gastrointestinal tract. In general, it is not toxic to man, except from chronic inhalation of MnO_2 during occupational exposure over long periods of time (2 years).⁽¹¹⁾

20. Mo (Molybdenum)

Molybdenum is required by bacteria, higher plants, and animals for a number of biological processes.

The accumulation of molybdenum by plants is proportional to the amount added to the soil. It is not toxic to plants at natural background levels.⁽³⁶⁾

It is concentrated by many freshwater and marine organisms including benthic algae, phytoplankton, zooplankton, molluscs,

crustaceans, insect larvae and fish.^(44,88) Molybdenum is also essential for the fixation of elemental nitrogen by bacteria and blue green algae.⁽⁸⁹⁾

Molybdenum exists in various valence forms. In mammals, the soluble hexavalent compounds are well absorbed from the gastrointestinal tract and transported to the liver. Ruminants are particularly sensitive to molybdenum which they may ingest while grazing.⁽⁹⁰⁾ A molybdenum concentration of 5 - 10 $\mu\text{g/g}$ is considered to be toxic to cattle.⁽⁸⁶⁾ Sheep, horses and swine are more tolerant to molybdenum.

Molybdenum accumulates in the kidneys and adrenals in humans. Excretion of molybdenum in man is rapid, occurring primarily in the urine. Excess molybdenum may be excreted in the bile. No data is available documenting molybdenum toxicity in man due to industrial exposure.⁽¹¹⁾

21. Ni (Nickel)

Little is known of either the soil chemistry or biological activity of nickel.⁽²⁾

Nickel is very toxic to many plants especially citrus fruits. At concentrations above 0.5 ng/l it will inhibit plant growth.⁽⁹¹⁾ Nickel is found in many soils in a generally insoluble form, but acidification may render it soluble causing plant injury or death. It now appears that the toxicity of nickel for plants may be caused by a decrease in the cation exchange capacity of the roots.⁽⁹²⁾

As a pure metal, nickel is not a problem in water pollution because it is not affected by, or soluble in water. Many nickel salts, however, are highly soluble in water.⁽³⁶⁾ Nickel salts can kill fish at very low concentrations. Data for the fathead minnow show death occurring in the range of 5 to 43 mg/l , depending upon the alkalinity of the water.⁽⁹³⁾ Little is known of the toxic effects of nickel in marine systems. However, nickel is toxic to phytoplankton and algae. Some marine animals have been found to contain up to 400 $\mu\text{g/l}$, and marine plants up to 3,000 $\mu\text{g/l}$ nickel.⁽³⁶⁾ The lethal limit of nickel has been reported as low as 0.8 mg/l for some marine fish, and 1.5 mg/l for juvenile oysters.⁽³⁶⁾

The chemical species of nickel greatly effects its toxicity to mammals. Nickel carbonyl, $\text{Ni}(\text{CO})_4$, is the most toxic of all

the nickel compounds to man. It causes death after exposure of 30 $\mu\text{g/g}$ for 30 minutes and has been implicated as a respiratory carcinogen.⁽¹¹⁾ Nickel carbonyl is formed when hot carbon monoxide is passed over nickel, both of which are waste products of coal fired power plants.

Dietary nickel is excreted by man largely in the feces, whereas nickel carbonyl is excreted in the urine.⁽¹¹⁾

As a particulate air pollutant, nickel has been found to have deleterious health effects in both humans and other mammals.⁽⁹⁴⁾

22. Pb (Lead)

Lead is present in all soils and plants. Soil contains an average of 10 to 15 $\mu\text{g/g}$ and ranges from 2 to 200 $\mu\text{g/g}$ of lead. The availability of lead in soils to plants is not understood. However, soil type and pH have been found to affect lead uptake. At low pH, lead is more available to plants. Plants are able to translocate lead from the soil to the roots but poorly transport it to the leaves and fruits. This occurs even when the soil lead is soluble and available in the soil.⁽⁹⁵⁾ For example, the lead content of strawberries does not change when the lead content of soil is increased from 8 to 59 $\mu\text{g/g}$. In radishes a ten-fold increase in soil lead content increases the lead concentration by a factor of less than two.⁽⁷⁷⁾ Thus it appears that soil lead may not be readily incorporated into the food chain via the soil plant pathway.

There is some evidence that lead may be phytotoxic as it has been shown to decrease transpiration and photosynthesis in sunflowers.⁽⁹⁶⁾

Roadside soils, plants earthworms, trout, and mice have been shown to have elevated lead levels which decrease rapidly with increasing distances from the highways.⁽⁹⁷⁻¹⁰⁰⁾

The toxicity of lead to freshwater organisms varies with its solubility which is a function of water hardness. For example, brook trout are adversely affected by lead at 0.10 ng/l in soft water, whereas in hard waters the 96 hour LC_{50} value is 442 mg/l .⁽³⁶⁾

Little is known of the biological effects of lead on marine organisms although the common marine mussel has been found to concentrate lead without showing detrimental effects.⁽¹⁰¹⁾ In addition some marine plants may concentrate lead up to 40,000 times.⁽³⁶⁾

Lead has many detrimental effects on humans which range greatly in severity. Acute toxicity, however, is most common in children.⁽¹¹⁾ Most lead enters man in the following components of the human diet: legumes (31%), garden fruits (19%), other fruits (16%), root vegetables (6%), grain and cereal (7%), meat, fish and poultry (7%), and leafy vegetables (5%).⁽⁴⁷⁾ The major routes of lead uptake in man are through the gastrointestinal tract and lungs. Of the lead ingested, 5 to 10% is absorbed and about 37% of the inhaled lead remains in the lungs. Once absorbed, lead accumulates primarily in the bones, with lesser amounts in other organs.⁽¹¹⁾

23. Rb (Rubidium)

Rubidium will substitute for potassium in many physiological processes in humans. Rubidium is well absorbed after oral administration, and is stored in the skeletal and cardiac muscle. There is no evidence that rubidium is toxic to man.⁽¹¹⁾

24. Sb (Antimony)

Little is known of the ecological effects of antimony. However, antimony may be concentrated by some marine organisms to levels above that present in sea water.⁽¹⁰²⁾

Antimony is slowly absorbed from the gastrointestinal tract in man. Trivalent forms of antimony concentrate in the red blood cells and the liver, and are slowly excreted, primarily in the feces. Pentavalent forms of antimony accumulate mainly in the blood plasma, liver and spleen, and are primarily released through the urine. It appears that antimony will not accumulate in man over long time periods. If heavy exposure does occur, symptoms similar to those of arsenic poisoning may result.⁽¹¹⁾ Chronic effects of antimony uptake in man are unknown. Some investigators have suggested a relationship between antimony and pulmonary carcinogenesis based on a possible antimony-containing abnormal enzyme system.⁽¹¹⁾

25. Sc (Scandium)

The oral toxicity of all of the rare earths is low in man due to poor gastrointestinal absorption.⁽¹¹⁾

26. Se (Selenium)

Selenium varies greatly in its soil concentration in the United States. Some areas of very high selenium content in the western U. S. have been purchased by the U. S. Government and removed from crop production. Other areas, such as in the north-east are deficient in selenium for good animal growth.⁽¹⁰³⁾ It would thus appear that additional selenium input, such as from the combustion of fossil fuels, might prove to be beneficial in certain parts of the country and deleterious in others.^(2, 103)

The soil chemistry of selenium is not understood, so that predictions of selenium uptake by plants from its soil concentration cannot reliably be made.⁽²⁾ In addition, selenium has not been shown to be essential for plant growth although it is concentrated by many plants to levels which are toxic to livestock.⁽¹⁰⁴⁾ For example, selenium at concentrations exceeding 200 $\mu\text{g/g}$ (dry weight) has been found in sweet clover growing on beds of fly ash.⁽¹⁰⁵⁾ It is stated that a concentration of selenium between 0.04 - 2 $\mu\text{g/g}$ is required to prevent deficiencies in cattle, whereas concentrations of 4 - 5 $\mu\text{g/g}$ are toxic.⁽¹⁰⁴⁾ The deficiency of selenium in mammals results in a degenerative muscle disease. Thus, selenium is essential to mammals, but within a very narrow range and may be so for man as well.

Information on the levels of selenium in freshwater and marine invertebrates and fish are limited; although it is known to concentrate in some seaweeds,⁽³⁶⁾ zooplankton,⁽¹⁰⁶⁾ invertebrates,⁽¹⁰⁷⁾ and fish.⁽¹⁰⁸⁾ It is believed that high selenium in fishes may result from high selenium content in the plankton upon which they feed.⁽¹⁰⁹⁾ In addition, the selenium concentration of some aquatic organisms has been correlated with those of mercury, arsenic, and thallium.⁽¹¹⁰⁾ All of these substances inhibit pulmonary selenium excretion. This has suggested a possible regulating process in the accumulation of these elements by marine organisms.⁽¹¹⁰⁾

Severe cases of livestock poisoning by selenium in waters have not been reported, although some spring and irrigation waters have been found to contain over 1 mg/l of selenium.⁽³⁶⁾ Very little is known of the potential toxicity of selenium to humans when ingested from water.⁽³⁶⁾

The human intake of selenium in food in seleniferous areas may range from 600 to 6,340 $\mu\text{g/day}$, which is stated to be close to the estimated levels at which symptoms of chronic selenium toxicity occur in man.^(36, 111) Chronic symptoms in man include

gastrointestinal distress, loss of hair and nails, and decayed teeth. Also reported are fetal and teratogenic effects, and fatty necrosis of the liver.⁽¹¹⁾ The toxicity of selenium to man depends upon its chemical species. Elemental selenium is probably not absorbed by the gastrointestinal tract. The highest concentration in man is found in the kidneys and hair, and mainly eliminated via the urine.⁽¹¹⁾ Most selenium enters the human diet through the ingestion of meat, fish and poultry (38%), and grain and cereal (62%).^(47,111)

27. Sn (Tin)

Very little is known about tin in the environment. Most investigations of the concentration of tin in plants have reported values below the level of detectability. This is believed to be due to low concentration of tin in soils.⁽¹¹²⁾ Recently, however, tin was shown to be concentrated by some plants collected near the tailings of a tin mine in Malaysia.⁽¹¹²⁾

Inorganic tin may be considered nontoxic to most organisms except at very high concentrations (500 µg/g for 14 months⁽¹¹⁾). Organic tin, however, is extremely toxic to mammals, including man.

In humans most of the ingested inorganic tin is not absorbed and ninety percent of this material is recovered in the feces. The absorbed inorganic tin concentrates in the liver and kidneys. Inhaled inorganic tin remains in the lungs, whereas organic tin may enter the blood stream and accumulate in the liver with smaller amounts entering other organs.⁽¹¹⁾

It has recently been shown that inorganic tin in both fresh water and marine sediments may be alkylated by bacterial action. The resulting organic species of tin may be volatilized and released into the atmosphere.⁽¹¹²⁾ Thus, tin remains a potential health and ecological threat.

28. Sr (Strontium)

The biological action and functions of strontium resemble those of calcium. Strontium may be essential for the growth of mammals, especially for the calcification of bones and teeth.⁽¹¹⁾

No adverse effects from the industrial use of strontium have been reported. Strontium is absorbed from the gastrointestinal

tract and is excreted in the urine and feces. Excess strontium is stored in the teeth and bones.⁽¹¹⁾

29. Te (Tellurium)

In general, the toxic effect of tellurium depends upon the particular compound and its dosage.⁽¹¹³⁾ Little else is known about the toxic effects of tellurium compounds, and it remains potentially dangerous.

Most tellurium is stored in bone, with some in the kidney. Urine is the principal route of excretion. Tellurium metal is of low toxicity to mammals, whereas tellurates and tellurites generally are moderately or highly toxic producing symptoms similar to those of arsenic poisoning. Serious cases of tellurium intoxication from industrial exposure have not been reported.⁽¹¹⁾

30. Tl (Thallium)

Thallium has been cited as having a very high pollution potential due to its reported toxicity to bacteria, higher plants and animals.⁽³⁰⁾

Little is known of its mode of action upon plants except that it has been reported to inhibit photosynthesis and transpiration.⁽⁹⁶⁾ There is practically no information available on the natural levels of thallium in aquatic biota or its toxicity.⁽¹¹⁴⁾ It is stated, however, to be lethal to fish at concentrations of 10-60 ng/l, to aquatic insects and invertebrates at 2-4 ng/l and to tad poles at 0.4 ng/l.⁽¹¹⁴⁾ Thallium has recently been reported to be as acutely toxic to juvenile Atlantic salmon as copper. It kills the young salmon very slowly allowing them to incorporate high gill liver and muscle concentrations prior to death.⁽¹¹⁵⁾ Thallium is also concentrated by some freshwater plants.⁽¹¹⁴⁾ There is no information on the effects on thallium compounds on marine organisms. Although it is reported to be concentrated by kelp⁽³⁶⁾, but not clams or mussels.⁽¹¹⁶⁾

Thallium is not a normal constituent of animal tissues. It is absorbed through the skin and gastrointestinal tract. In humans, most thallium accumulates in the kidney, with lesser amounts in other tissues. Thallium is excreted slowly through the urine, with small amounts in the feces.⁽¹¹⁾ Thallium is quite toxic, with a lethal dose for humans estimated to be 8 to 12 µg/g. Rat studies have indicated that thallium oxide is more toxic when taken orally than when administered by injection.⁽¹¹⁾ Thallium

oxide is believed to be the main species of thallium released by the combustion of coal.⁽¹⁾

31. Ti (Titanium)

Approximately 3% of an oral dose of titanium is absorbed by man, and of that, most is excreted via the urine. The metal, salts, and oxides of titanium are all non-toxic to man, and in most cases, are considered physiologically inert.⁽¹¹⁾

32. U (Uranium)

There are no data on the concentration of uranium compounds by fresh water and marine organisms. In addition, the data that are available suggest that uranyl salts are somewhat less toxic to marine than to fresh water organisms.⁽³⁶⁾

Inhalation of uranium dioxide dust at a concentration of 5 mg/m³ for five years produces no evidence of toxicity in mammals. However, uptake of the soluble uranyl ion may result in acute renal damage.⁽¹¹⁾

33. V (Vanadium)

Vanadium is ubiquitous in the environment. There is some evidence that vanadium is useful and possibly essential in both mammalian and some plant systems.^(11,117)

Vanadium is usually found in low concentrations in most soil materials, although it ranges from 20-500 µg/g.⁽²⁾ Vanadium enters the atmosphere through the combustion of petroleum derivatives and coal, and then settles out on the earth's surface including the oceans.⁽³⁶⁾ The ash of some oils, in fact, has been stated to contain more than 70% vanadium oxide.⁽¹¹⁸⁾ Thus, vanadium can serve as a useful indicator of the presence of other pollutants in the environment which are associated with the combustion of fossil fuels.

Vanadium has been shown to accumulate in forest litter, humus, lichens, mosses and the needles of spruce trees.⁽¹¹⁹⁾ However, when present in plant culture solutions at concentrations of 0.5 µg/g or greater, vanadium is toxic to some plants.⁽¹²⁰⁾ The accumulated vanadium, in general, remains in the roots of plants with very little reaching the stem and leaves. It is stated that plant shoots seldom contain more than 1 µg/g of vanadium.⁽²⁾

Information on the occurrence of vanadium in freshwater biota is lacking. There are also no reports in the literature on the toxicity of vanadium to marine organisms. However, several species of marine algae,⁽¹²¹⁾ invertebrate ascidians⁽¹²²⁾ and tunicates⁽¹²³⁾ concentrate vanadium to very high levels.

Vanadium has a very low order of oral toxicity to mammals. It does not affect growth, life span, nor does it produce tumors in rats or mice when given in concentrations of 5 mg/l in their dietary water.⁽⁵⁵⁾

In humans, vanadium is excreted primarily by the kidneys. The toxic action of vanadium is largely confined to the respiratory tract. At very high concentrations (industrial exposure), gastrointestinal disorders, kidney damage, and cardiac palpitations have been observed. Heart disease has also been postulated to be related to the vanadium concentration in the air.⁽¹¹⁾

34. W (Tungsten)

There are no reports of tungsten toxicity to either terrestrial or aquatic biota. Tungsten is usually not found in animal tissue. It is absorbed by the gastrointestinal tract, and retained in the bone, with lesser amounts retained in the spleen, liver and kidney. Oral toxicity does not appear to be a problem. Tungsten may be antagonistic to the uptake of molybdenum.⁽¹¹⁾

35. Zn (Zinc)

Zinc has been shown to be essential for the growth and normal development of microorganisms, plants and animals, and is thus accumulated by most organisms.

Zinc is generally uniformly distributed throughout the soil profile.⁽²⁾ Zinc deficiency occurs in soils in most of the agricultural areas of the United States.⁽¹²⁴⁾ Plants vary greatly in their ability to assimilate zinc from the soil. Tissues of plants deficient in zinc usually contain less than 15-20 µg/g zinc while plant tissues containing an excess of 400 µg/g zinc show toxicity symptoms.^(2,125) Lichens, in particular, are very sensitive to zinc and may serve as indicators of excessive zinc in the environment.⁽¹²⁶⁾

According to the Environmental Protection Agency, in zinc mining areas, zinc has been found in waters in concentrations as high as 50 mg/l, and in effluents from metal plating works and

small arms ammunition plants it may occur in significant concentrations. In most surface and ground waters, it is present only in trace amounts. There is some evidence that zinc ions are adsorbed strongly and permanently on silt, resulting in the inactivation of the metal.⁽¹²⁸⁾ Concentrations of zinc in excess of 5 mg/l in raw water used for drinking water produces an undesirable taste which persists through conventional treatment.⁽¹²⁸⁾

The acute toxicity of zinc to freshwater organisms varies greatly with the water hardness, dissolved oxygen concentration, pH, and temperature. Resistance to zinc toxicity varies between species, and may be different for juvenile and adult forms.⁽¹²⁹⁾ For example, zinc was found to be most toxic to freshwater minnows at a pH of 8 and hardness of 50 $\mu\text{g/g}$ and least toxic at pH of 6 and hardness of 200 $\mu\text{g/g}$.⁽¹³⁰⁾ The presence of copper in water may also increase the toxicity of zinc to aquatic organisms.⁽¹²⁸⁾

It is stated that the main concern of zinc compounds in marine waters is not one of acute toxicity, but rather the long term sub-lethal effects of the metallic compounds and complexes.⁽³⁶⁾ Invertebrate marine organisms are reported to be more sensitive than vertebrates to acute zinc toxicity.⁽³⁶⁾ Most marine organisms often concentrate zinc to levels greatly above that present in seawater.⁽¹³¹⁾

While an increase in zinc intake in rats results in an increase in the concentration of zinc in their tissues, its accumulation is not great and levels fall rapidly soon after the termination of the experiment.⁽¹³²⁾

In humans, zinc is concentrated in the muscle, liver, kidney, and pancreas, and is eliminated by the gastrointestinal tract. Zinc has been shown to be antagonistic to the detrimental effects of cadmium. Exposure to high concentrations of zinc oxide fumes results in fever in man, but this usually disappears within 24 to 48 hours.⁽¹¹⁾ In general, zinc is a required nutrient by man and can be considered essentially harmless except when administered in very high dosages. Most zinc enters the human diet through the ingestion of meat, fish and poultry (37%), dairy products (21%), grain and cereal (19%), and potatoes (7%).⁽⁴⁷⁾

REFERENCES

1. Cavanaugh, G., C. E. Burklin, J. C. Dickerson, H. E. Lebowitz, S. S. Tam, G. R. Smithson, H. Nack, and J. H. Oxley
Potentially Hazardous Emissions from the Extraction and Processing of Coal and Oil
USEPA Report EPA-650/2-75-038, p. I-154 (1975)
2. Berry, W. L. and A. Wallace
Trace Elements in the Environment - Their Role and Potential Toxicity as Related to Fossil Fuels
A Preliminary Study Report Prepared by the University of California, Laboratory of Nuclear Medicine and Radiation Biology for the Atomic Energy Commission, pp. 1-66 (1974)
3. Bertine, K. K. and E. D. Goldberg
Fossil Fuel Combustion and the Major Sedimentary Cycle Science, 173, 223-235 (1971)
4. Herbees, S. E., G. R. Southworth, and C. W. Gehrs
Organic Contaminants in Aqueous Coal Conversion Effluents: Environmental Consequences and Research Priorities
Oak Ridge National Laboratory Report # 880 (1976)
5. Freudenthal, R. I., G. A. Lutz, and R. I. Mitchell
Carcinogenic Potential of Coal and Coal Conversion Products
Battelle Columbus Laboratories, Energy Program Report, pp. 1-34 (1975)
6. Vaughan, B. E., K. H. Abel, D. A. Cataldo, J. M. Hales, C. E. Hane, I. A. Rancitelli, R. C. Roatson, R. E. Wildung, and E. G. Wolf
Review of Potential Impact on Health and Environmental Quality from Metals Entering the Environment as a Result of Coal Utilization
Battelle Pacific Northwest Laboratories Energy Program Report, pp. 1-75 (1975)
7. Newkirk, H. W.
Environmental Effects of Energy Production and Utilization in the U. S. Volume 1: Sources, Trends and Costs of Control
Lawrence Livermore Laboratory Report UCRL-51930, pp. 1-452 (1976)

8. Klein, D. H., A. W. Andren, J. C. Carter, J. F. Emery, C. Feldman, W. Fulkerson, W. S. Lyon, J. C. Ogle, Y. Talmi, R. I. Van Hook, and N. Bolton
Pathways of Thirty Seven Trace Elements Through a Coal Fired Power Plant
Envir. Sci. Tech., 9, 973-979 (1975)
9. Klein, D. H. and P. Russell
Heavy Metals Fallout Around a Power Plant
Envir. Sci. Tech., 7, 357-358 (1973)
10. Ruch, R. R., H. J. Gluskofer, and N. F. Shimp
Occurrence and Distribution of Potentially Volatile Trace Elements in Coal
Illinois State Geological Survey, Environmental Geology Notes No. 72 (1974)
11. Beliles, R. P.
Metals
In: Toxicology - The Basic Science of Poisons, pp. 454-502
L. J. Casarett and J. Doull (Editors)
Macmillan, NY (1975)
12. New Kirk, H. W.
Environmental Effects of Energy Production and Utilization in the U. S. Volume 2: Public Health Effects
Lawrence Livermore Laboratory Report UCRL-51930, pp. 1-120 (1976)
13. Schroeder, H. A.
The Biological Trace Elements
J. Chronic Dis., 18, 217-228 (1965)
14. Schroeder, H. A. and Mitchener, M.
Toxic Effects of Trace Elements on the Reproduction of Mice and Rats
Arch. Envir. Health, 23, 102-106 (1971)
15. Dulka, J. J. and T. H. Risby
Ultratrace Metals in Some Environmental and Biological Systems
Anal. Chem., 48, 642-653 (1976)
16. Comar, C. L. and N. Nelson
Health Effects of Fossil Fuel Combustion Products: Report of a Workshop
Envir. Health Perspect., 12, 149-170 (1975)

17. Rhodes, W. J.
Potential Pollutants in Coal and the Environmental Impact of
Gasification
USEPA Report (1973)
18. Allaway, W. H.
Agronomic Controls Over the Environmental Cycling of Trace
Elements
A. G. Norman (Editor)
Advances in Agronomy, 20, 235-274 (1968)
19. Klein, D. H. and A. A. Andren
Trace Element Discharges from Coal Combustion for Power
Production
Water Air Soil Poll., 5, 71-77 (1975)
20. Lindberg, S. E., A. W. Andren, R. J. Raridon, and W. Fulkerson
Mass Balance of Trace Elements in Walker Branch Watershed -
The Relation to Coal Fired Steam Plants
Presented at Third Annual Research Triangle Conference on
Heavy Metals in the Environment, pp. 1-28 (1975)
21. Ragaini, R. C. and J. M. Ondov
Trace Contaminants from Coal Fired Power Plants
Lawrence Livermore Laboratory Report UCRL-76794 (1975)
22. Hall, H. J., G. M. Varga, and E. M. Magee
Trace Elements and Potential Pollutant Effects in Fossil Fuels
F. A. Ayer (Editor)
Symposium Proceedings - Environmental Aspects of Fuel Conver-
sion Technology, EPA 650/2-74-118, pp. 35-47 (1974)
23. Bolton, N. E., R. I. Van Hook, W. Fulkerson, W. S. Lyon, A. W.
Andren, J. A. Carter, and J. F. Emery
Trace Element Measurements at the Coal Fired Allen Steam Plant
Progress Report June 1971 - January 1973
Oak Ridge National Laboratory Report ORNL-NSF-EP-43, pp. 1-83
(1973)
24. Bolton, N. E. et al.
Trace Element Measurements at the Coal Fired Allen Steam Plant
Progress Report February 1973 - July 1973
Oak Ridge National Laboratory Report ORNL-NSF-EP-62, pp. 1-43
(1974)

25. Lee, R. E., Jr., H. L. Crist, A. E. Riley, and K. E. MacLead
Concentration and Size of Trace Metal Emissions from a Power
Plant, a Steel Plant and a Cotton Gin
Envir. Sci. Tech., 9, 643-647 (1975)
26. Natusch, D. F. S. and J. R. Wallace
Toxic Trace Elements: Preferential Concentrations in Respirable
Particles
Science, 183, 202 (1974)
27. Davidson, R. L., D. F. S. Natusch, and J. R. Wallace
Trace Elements in Fly Ash
Envir. Sci. Tech., 8, 1107-1113 (1974)
28. Klein, D. H. and P. Russell
Heavy Metals: Fallout Around a Power Plant
Envir. Sci. Tech., 7, 357-358 (1973)
29. Lisk, D. J.
Trace Metals in Soils, Plants and Animals
Adv. in Agron., 24, 267-325 (1972)
30. Bowen, H. J.
Trace Elements in Biochemistry
Academic Press, London (1966)
31. Proposed Criteria for Water Quality, Vol. I, pp. 1-425
U. S. Environmental Protection Agency, Washington, DC (1973)
32. McKee, J. E. and H. W. Wolf (Editors)
Water Quality Criteria, 2nd Edition
The Resources Agency of California State Water Quality Board,
Sacramento, CA, Publication No. 3-A (1963)
33. Wilber, C. D.
The Biological Aspects of Water Pollution, p. 296
Charles Thomas Publisher (1971)
34. Thompson, S. E., C. A. Burter, D. J. Quinn and Y. C. Ng
Concentration Factors of Chemical Effluents in Edible Aquatic
Organisms
Lawrence Livermore Laboratory Report UCRL-50564 (1972)

35. Wood, J. M.
The Chemical Toxicity of Elements
Science, 183, 1049-1051 (1974)
36. Proposed Criteria for Water Quality, Vol. I, pp. 1-425
U. S. Environmental Protection Agency, Washington, D. C. (1973)
37. Thurberg, F. P. and R. S. Collier
Respiratory Response of Cunnners to Silver
Marine Pollut. Bull., 8, 40-41 (1977)
38. Schroeder, H. A. and J. J. Balassa
Abnormal Trace Metals in Man: Arsenic
J. Chron. Diseases, 19, 85-106 (1966)
39. Bazzaz, F. A., R. W. Carlson and G. I. Rolfe
The Effect of Heavy Metals on Plants: Pt. I, Inhibition of
Gas Exchange in Sunflowers by Pb, Cd, Ni, and Tl
Environ. Pollu., 7, 241-246 (1974)
40. Porter, E. K., and P. J. Peterson
Arsenic Accumulation by Plants on Mine Waste
Sci. Total. Environ., 4, 365 (1975)
41. Penrose, W. R.
Arsenic in the Marine and Aquatic Environment: Analysis,
Occurrence, and Significance
CRC Critical Reviews in Environmental Control, 4, 465-482 (1972)
42. Schuth, C. K., A. R. Isensee, E. A. Woolson, and P. C. Kearney
Distribution of ^{14}C and Arsenic Derived from ^{14}C - Cacodylic
Acid in an Aquatic Ecosystem
J. Agr. and Food Chem., 22, 999-1003 (1974)
43. Woolson, E. A., P. G. Kearney, A. R. Isensee, W. G. McShane,
K. J. Irgolic, and R. A. Zingaro
Bound Arsenic Fraction in a Crustacean
168th ACS Meeting (1974)
44. Lowman, F. G., T. R. Rice, and F. A. Richards
Accumulation and Redistribution of Radionuclides by Marine
Organisms
In: Radioactivity in the Marine Environment, pp. 161-191
National Academy of Sciences, Washington, D.C. (1971)

45. Frost, D. V.
Arsenicals in Biology - Retrospect and Prospect
Fed. Proc., 26, 208 (1967)
46. Buchanan, W. D.
Toxicity of Arsenic Compounds
Elsevier Publishing Co., New York (1962)
47. Mahaffey, K. R.
Heavy Metal Exposure from Foods
Environ. Health Perspec., 12, 63-69 (1975)
48. McKee, J. E., and H. W. Wolf (Editors)
Water Quality Criteria, 2nd ed., p. 548
California State Water Quality Control Board, Sacramento (1963)
49. Moiseev, P. A., and A. V. Kardashev
Radioactivity of Certain Marine Life
In: Radioactive Contamination of the Sea
Academy of Sciences, USSR, Moscow (1964)
50. Haas, A. R. C.
Nutritional Aspects of Mottleleaf and Other Physiological
Diseases of Citrus
Hilgardia, 6, 483-559 (1932)
51. Romney, E. M., and J. D. Childress
Effects of Beryllium in Plants and Soil
Soil Sci., 100, 210-217 (1965)
52. Romney, E. M., J. D. Childress, and G. V. Alexander
Beryllium and the Growth of Bush Beans
Science, 135, 786 (1962)
53. Ballard, E. G., and G. W. Butler
Mineral Nutrition of Plants
Ann. Rev. Plant. Physiol., 17, 77-112 (1966)
54. Goldberg, E. D., W. S. Broecker, M. G. Gross, and K. K.
Turekian
Marine Chemistry
In: Radioactivity in the Marine Environment, pp. 137-146
National Academy of Sciences, Washington, D.C. (1971)

55. Schroeder, H. A.
Metals in the Air
Environment, 13, 18-32 (1971)
56. Stenström, T.
Cadmium Availability to Wheat: A Study with Isotope Tracers
Under Field Conditions
Ambio, 3, 87-90, 1974
57. Nilsson, R.
Aspects of the Toxicity of Cadmium and Its Compounds
Bull. 7, p. 58, Ecological Research Committee, Swedish Natural
Science Council Stockholm, Sweden (1970)
58. Matti, C. S. et al.
Cycling of Hg and Cd in an Old Field Ecosystem During One
Growing Season
Oak Ridge National Lab. Report ORNL-NSF-EATC 10
Environ. Sci. Div. Publication No. 641 1-75 (1975)
59. John, M. K., C. J. Van Laerhoven, and H. H. Chuah
Factors Affecting Plant Uptake and Phytotoxicity of Cadmium
Added to Soils
Environ. Sci. Tech., 6, 1005-1009 (1972)
60. Hutchinson, T. C. and Czyrska, H.
Cadmium and Zinc Toxicity and Synergism to Floating Aquatic
Plants
Water Poll. Res., 7, 59-65 (1972)
61. Lucas, H. F., Jr., D. N. Edgington, and P. J. Colby
Concentrations of Trace Elements in the Great Lakes' Fishes
J. Fish. Res. Bd. Canada, 27, 677-684 (1970)
62. Greig, R. A., A. E. Adams, and B. A. Nelson
Uptake of Cadmium by Organs and Tissues
In: Physiological Response of the Cunner, Tautogolabrus
adspersus to Cadmium
NOAA Technical Report NMFS SSRF-681, pp. 5-9 (1974)
63. Pringle, B. H., D. E. Hissong, E. L. Katz and S. T. Mulawka
Trace Metal Accumulation by Estuarine Mollusks
J. Sanit. Eng., 94, 455-475 (1968)

64. Brooks, B. R. and M. G. Rumsby
The Biogeochemistry of Trace Element Uptake by Some New Zealand Bivalves
Limnol. Oceanog., 10, 521-527 (1965)
65. Lake, P. S. and V. J. Thorp
The Gill Lamellae of the Shrimp Paratya tasmaniensis
Normal Ultrastructure and Charges with Low Levels of Cadmium,
Vol. II, pp. 448-449
Eighth International Congress on Electron Microscopy, Canberra
(1974)
66. Miller, W. J.
Cadmium Absorption, Tissue and Product Distribution, Toxicity
Effects and Influence on Metabolism of Certain Essential
Elements, pp. 58-50
In: Proceedings Georgia Nutrition Conference, University of
Georgia, Athens (1971)
67. Yamagata, N. and I. Shigamatsu
Cadmium Pollution in Perspective
Inst. of Public Health Tokyo, Bull, 19, 1-27 (1970)
68. Kubota, J., E. R. Lemon, and W. H. Allaway
The Effect of Soil Moisture Content Upon the Uptake of Molybdenum,
Copper, and Cobalt by Alsike Clover
Soil Science Amer. Proc., 27, 679 (1963)
69. Krickenberger, K. R.
Development Document for Effluent Limitations Guidelines and
New Source Performance Standard for the Cu, Ni, Cr, and Zn
Segment of the Electroplating Point Source Category
EPA Report, pp. 1-21 (1974)
70. Mertz, W.
Biological Role of Chromium
Fed. Proc., 26, 186 (1967)
71. Saward, D., A. Stirling, and G. Topping
Experimental Studies on the Effects of Copper on a Marine Food
Chain
Mar. Biol., 29, 351-361 (1965)

72. Liebig, G. F., Jr., A. P. Vanselow, and H. D. Chapman
Effects of Aluminum on Copper Toxicity, as Revealed by Solution -
Culture and Spectrographic Studies of Citrus.
Soil Sci., 53, 341-351 (1942)
73. Prival, M. J. and Friber, F.
Fluoride in the Air
Environment, 15, 25 (1973)
74. Groth, E.
An Evaluation of the Potential for Ecological Damage by Chronic
Low Level Environmental Pollution by Floride, pp. 224-240
ISIR Conference (1974)
75. Underwood, E. J.
Trace Elements in Human and Animal Nutrition, 3rd ed.
Academic Press, Inc., New York (1971)
76. Abelson, P. H.
Methylmercury
Science, 169, 1 (1970)
77. Ratsch, H. C.
Heavy Metal Accumulation in Soil and Vegetation from Smelter
Emissions
EPA Report 66013-74-012, pp. 1-23 (1974)
78. Huckabee, J. W., and N. A. Griffith
Toxicity of Hg and Se to the Eggs of Carp, Cyprinus Carpio
Trans. Amer. Fish Soc., 103, 822-825 (1974)
79. Hess, L. W., R. L. Brown, and J. F. Heisinger
Mercury Contamination of Birds from a Polluted Watershed
J. Wildlife Management, 39, 299-304 (1975)
80. Doudoroff, P.
Water Quality Requirements of Fishes and Effects of Toxic
Substances
In: The Physiology of Fishes, pp. 403-430
M. E. Brown (Editor)
Academic Press, N. Y. (1952)
81. Doudoroff, P., and M. Katz
Critical Review Literature on the Toxicity of Industrial
Wastes Toxic Compounds to Fish
Sewage and Industrial Wastes, 22, 1432 (1961)

82. Krenkel, P. A.
Mercury: Environmental Considerations
CRC Crit. Rev. Environ. Con, pp. 251-339 (1974)
83. Water Quality Criteria Data Book
Arthur D. Little Inc. for U. S. EPA 18010DPV12/70 (1970)
84. Stopford, W., and L. J. Goldwater
Methylmercury in the Environment: A Review of Current Understanding
Environ. Health Perspective, 12, 115-118 (1975)
85. Hannerz, L.
Experimental Investigations on the Accumulation of Mercury in Water Organisms
Rept. Inst. Freshwater Res., Drottningholm, Sweden, 48, 120-176 (1968)
86. Gather, H. E., C. Goudie, M. L. Sunde, M. J. Kopecky, P. Wagner, S. Oh, and W. G. Hoekstra
Selenium: Relation to Decreased Toxicity of Methylmercury Added to Diets Containing Tuna
Science, 175, 1122-1124 (1972)
87. Koeman, J. H., W. S. M. Van de Ven, J. J. M. Goeij, P. S. Tjoe, and J. L. Van Haafren
Mercury and Selenium in Marine Mammals and Birds
Science Total Environ., 3, 279-287 (1975)
88. Florkin, M., and G. Duchateau
Sur la Distribution Zoologique de la Xanthine Oxydase
Bull. Classe Sci. Acad. Roy. Belg., 27, 174-178 (1941)
89. Hardy, R. W. F., and C. R. Burns
Biological Nitrogen Fixation
Ann. Rev. Biochem., 37, 331-358 (1968)
90. Kubota, J. V., A. Lazar, G. H. Simonson, and W. W. Hill
The Relationship of Soils to Molybdenum Toxicity in Grazing Animals in Oregon
Soil Sci. Soc. Am. Proc., 31, 667-671 (1967)

91. Vanselow, A. P.
Nickel
In: Diagnostic Criteria for Plants and Soils, pp. 302-309
H. D. Chapman (Editor)
University of California, Berkeley (1966)
92. Preliminary Investigation of Effects on the Environment of
Boron, Indium, Nickel, Selenium, Tin, Vanadium, and Their
Compounds, Volume III Nickel
U. S. EPA Report EPA-560/2-75-005C, pp. 1-89 (1975)
93. Pickering, Q. H., and C. Henderson
The Acute Toxicity of Some Heavy Metals to Different Species
of Warm Water Fishes
J. Air Wat. Pollut., 10, 453-463 (1966)
94. Graham, J. A.
Effect of Nickel Chloride on Primary Antibody Production in
the Spleen
Environ. Hlth. Perspect., 12, 109-113 (1975)
95. John, M. K.
Lead Availability Related to Soil Properties and Extractable
Lead
J. Environ. Qual., 1, 295-298 (1972)
96. Bazzaz, F. A., R. W. Carlson, and G. L. Rolfe
The Effect of Heavy Metals on Plants: Part I. Inhibition of
Gas Exchange in Sunflowers by Pb, Cd, Ni and Tl
Environ. Pollut., 7, 241-246 (1974)
97. Motto, H. L., R. H. Daines, D. M. Chilko, and C. K. Motto
Lead in Soils and Plants: Its Relationship to Traffic Volume
and Proximity to Highways
Environ. Sci. Technol., 4, 231-237 (1970)
98. Welch, W. R. and D. L. Dick
Lead Concentrations in Tissues of Roadside Mice
Environ. Pollut., 8, 15-21 (1975)
99. Pagenkopf, C. K., and D. R. Neuman
Bull. Environ. Contam. Toxicol., 12, 70-75 (1974)

100. Gish, C. D. and R. E. Christensen
Cadmium, Nickel, Lead, and Zinc in Earthworms from Roadside
Soil
Environ. Sci. Technol., 7, 1060-1062 (1973)
101. Schulz-Baldes, M.
Lead Uptake from Seawater and Food and Lead Loss in the
Common Mussel Mytilus Edulis
Mar. Biol., 25, 177-193 (1974)
102. Goldberg, E. D.
Biochemistry of Trace Metals
In: Treatise on Marine Ecology and Paleoecology
J. W. Hedgpeth (Editor)
Geological Society of America Memoir No. 67, pp. 345-357 (1957)
103. Andren, A. W., and D. H. Klein
Selenium in Coal Fired Steam Plant Emissions
Environ. Sci. Technol., 9, 856-858 (1975)
104. Allaway, W. H.
Control of the Environmental Levels of Selenium in "Trace
Substances"
Environmental Health 2, pp. 181-205
D. D. Hemphil (Editor)
Proc. Univ. Missouri Annual Conf., Univ. of Missouri, Columbia
(1969)
105. Gutenmann, W. H., and C. A. Bache
Selenium in Fly Ash
Science, 191, 966-967 (1975)
106. Copeland, R.
Selenium: The Unknown Polutant
Limnos, 3, 7-9 (1970)
107. Fowler, S. W. and G. Benayoun
Influence of Environmental Factors on Selenium Flux in Two
Marine Invertebrates
Mar. Biol., 37, 59-68 (1976)
108. Chau, Y. K. and J. P. Riley
The Determination of Selenium in Seawater, Silicates and
Marine Organisms
Anal. Chim. Acta, 33, 36-49 (1965)

109. Sandholm, M., H. E. Oksanen, and L. Pesonen
Uptake of Selenium by Aquatic Organisms
Limnol. Oceanog., 18, 496-499 (1974)
110. MacKay, N. J., M. N. Kazcos, R. J. Williams, and M. I. Leedow
Selenium and Heavy Metals in Black Marlin
Mar. Pollut. Bull., 6, 57-61 (1975)
111. Morris, V. C., and O. A. Levander
Selenium Content of Foods
J. of Nutrition, 100, 1385-1388 (1970)
112. Peterson, P. J., M. A. S. Butron, M. G. Gregson, S. M. Nye,
and E. K. Porter
Tin in Plants and Surface Waters in Malaysian Ecosystems
Presented at 10th Annual Symposium - Trace Substances in the
Environment, Columbia, Missouri, pp. 1-14 (1976)
113. Devlin, T.
A Review of the Toxicology of Tellurium and Its Compounds
Sandia Labs. Rept. SAND 75-8045 (1975)
114. Zitko, V., W. V. Carson, and W. G. Carson
Thallium: Occurrence in the Environment and Toxicity to Fish
Bull. Environ. Contam. Toxicol., 13, 23-30 (1975)
115. Zitko, V.
Toxicity and Pollution Potential of Thallium
The Science of the Total Environment, 4, 185-192 (1975)
116. Zitko, V., and W. V. Carson
Accumulation of Thallium in Clams and Mussels
Bull. Environ. Contam. Toxicol., 14, 530-533 (1975)
117. Arnon, D. I., and G. Wessel
Vanadium as an Essential Element for Green Plants
Nature, 172, 1039-1040 (1953)
118. Goldschmidt, V. M.
Geochemistry, pp. 1-912
A. Muir (Editor)
Oxford Univ. Press (1954)

119. Rühling, Å., and G. Tyler
Heavy Metal Pollution and Decomposition of Spruce Needle
Litter
Oikos, 24, 402-416 (1973)
120. Pratt, P. F.
Vanadium
In: Diagnostic Criteria for Plants and Soils, pp. 136-141
H. D. Chapman (Editor)
Univ. of Calif., Div. of Agr. Sci. (1966)
121. Vinogradov, A. P.
The Elementary Chemical Composition of Marine Organisms
Sears Foundation for Marine Research, Yale University,
Memoir No. 2 (1953)
122. Swinehart, J. H., W. R. Biggs, D. J. Halko, and N. C. Schroeder
The Vanadium and Selected Metal Contents of Some Ascidians
Biol. Bull., 146, 302-312 (1974)
123. Goldberg, E. D., W. McBlair, and K. M. Taylor
The Uptake of Vanadium by Tunicates
Biol. Bull., 101, 84-94 (1951)
124. Beeson, K. C.
Yearbook of Agriculture, Soils, pp. 258-267
U.S.D.A. (1957)
125. Chapman, H. D.
Zinc
In: Diagnostic Criteria for Plants and Soils
H. D. Chapman (Editor)
Univ. of Calif., Div. of Agr. Sci. (1966)
126. Nash, T. H.
Influence of Effluents from a Zinc Factory on Lichens
Ecological Monographs, 45, 183-198 (1975)
127. Krickenberger, K. R.
Development Document for Effluent Limitations Guidelines and
New Source Performance Standards for the Cu, Ni, Cr, and
Zn Segment of the Electroplating Point Source Category
U. S. Environmental Protection Agency, pp. 1-21 (1974)

128. Skidmore, J. F.
Toxicity of Zinc Compounds to Aquatic Animals with Special
Reference to Fish
Quart. Rev. Biol., 39, 227-248 (1964)
129. Mount, D. I.
The Effect of Total Hardness and pH on Acute Toxicity of
Zinc to Fish
Air Wat. Pollut. Int. J., 10, 49-56 (1966)
130. Ketchum, B. H., and V. T. Bowen
Biological Factors Determining the Distribution of Radio-
isotopes of the Sea
In: Proc. 2nd Int. Conf. of the Peaceful Uses of Atomic
Energy, United Nations Geneva, September 1-13, 18,
429-433 (1958)
131. Drinker, K. R., P. K. Thompson, and M. Marsh
Investigation of the Effect Upon Rats of Long-Continued
Ingestion of Zinc Compounds, with Special Reference to
the Relation of Zinc Excretion to Zinc Intake
American J. Physiol., 81, 284-306 (1927)

TABLE 1

TOXIC AND POTENTIALLY TOXIC SUBSTANCES RELEASED INTO
THE ENVIRONMENT DURING COAL COMBUSTION
(References 1-10)

Group	Examples
1. Acids and Anhydrides	Maleic Anhydride Sulfuric Acid Benzoic Acid Nitric Acid Hydrochloric Acid
2. Amines	Ammonia Aliphatic Amines α and β Naptithyl Amines Aniline Methylaniline Benzidine
3. Inorganic Salts	Chromium Chloride Chromium Sulfide
4. Carbonyl Compounds	Formaldehyde Acetaldehyde
5. Heterocyclics	Pyridines Quinolines
6. Hydrocarbons	Benzene Toluene Xylene Aliphatics Olephins
7. Phenols	Phenols Cresols Xylanols
8. Polycyclic Aromatic Hydrocarbons	Benzo(a)pyrene Dibenzoflourene Dibenzoanthracene Benzoanthracenes Benzo(a)anthrone Dimethylbenzoanthracene

TABLE 1 (Cont'd)

Group	Examples
	Chrysene Methylchrysenes Benzocarbazoles Indenopyrenes Carbazoles Pyrenes Biphenyl Acenaphthalene Acenaphthalene Flourene Alkylanthracenes Alkylphenanthracenes Anthracene Perylene Benzoperylene Coronene
9. Sulfur Compounds	Thiophenes Hydrogen Sulfide Mercaptans Carbon Disulfide Carbonyl Sulfide Methyl Thipene
10. Trace Elements	Antimony Arsenic Barium Beryllium Bismuth Cadmium Chromium Cobalt Copper Fluorine Gallium Lead Manganese Mercury Molybdenum Nickel Selenium

TABLE 1 (Cont'd)

Group	Examples
11. Organometallics	Silver Tellurium Thallium Tin Uranium Vanadium Zinc
12. Fine Particulates	Nickel Carbonyl Tetraethyl Lead Sulfur Particulates Respirable Coal Dusts Tar Soot
13. Gases	CO SO ₂ SO ₃ SO ₄ NO
14. Cyanides	Hydrogen Cyanide Ammonium Cyanide Naphthyl Cyanide Ammonium Thiocyanate

TABLE 2
SUMMARY OF TRACE ELEMENT EFFECTS ON HUMANS AND MAMMALS
(References 11-16)

Element	Human Body Burden (mg/70 kg)	Human Daily Intake (ng)	Human Target Organs	Suspected or Known Carcinogen via Inhalation or Ingestion	Toxic Effects on Humans Other than Cancer	Essential for Mammals	Reproductive Effects on Mammals	LD ₅₀ Mammals
Ag	<1	-	Skin	-	Argyria	-	-	0.008 g/kg (rabbit)
As	<100	0.7	Respiratory System, G.I. Tract, CNS, Liver, Skin, Blood, Endocrine System	Cancer of mouth, Esophagus, Larynx, Bladder	Poisoning of oxidative phosphorylation system	-	Reduced litter size urogenital abnormalities	0.07 g/kg (rat)
B	<10	0.01-0.02	G.I. Tract	-	-	-	-	-
Ba	16	16	G.I. Tract, Respiratory System, CNS, CVS, Skin	-	Highly toxic when ingested	-	-	0.07 g/kg (mouse)
Be	-	-	Respiratory System, Skin, Bone	Possible Carcinogen in lungs and bones	Skin damage	-	-	0.0005 g/kg (mouse)
Cd	30	0.016-0.20	G.I. Tract, Respiratory System, CNS, CVS, Liver, Skin, Kidney	Carcinomas in lungs	Hypertension, Pulmonary Emphysema, Kidney damage	-	Runting, failure to reproduce	0.027 g/kg (mouse)
Co	1	0.3	G.I. Tract, Respiratory System, CNS, CVS, Skin, Endocrine System	-	-	-	-	0.5 g/kg (rat)
Cr	<6	0.06	Respiratory System	Cancer of Respiratory tract (Cr ^{VI})	Emphysema, Pneumonia	(Cr ⁺³)	-	0.18 g/kg (rat)
Cu	100	3.2	G.I. Tract, Blood	-	-	+	-	0.05 g/kg (mouse)
Fe	4,100	15	G.I. Tract, Respiratory System, CNS, CVS, Blood, Endocrine System	-	-	+	-	0.9 g/kg (rat)
Ga	-	-	Kidney, Liver, Muscles	Linked to tumor formation	Neuromuscular poison, kidney damage	-	-	0.05 g/kg (rat)
Ge	Trace	1.5	G.I. Tract, Respiratory System, CVS	-	-	-	-	-
Hg	Trace	0.02	Respiratory System, CNS, CVS, Liver, Kidney	-	Central Nervous System poison	-	Neuromuscular abnormalities, CNS changes	0.027 g/kg (mouse)
In	-	-	Kidney	-	-	-	-	0.003 g/kg (rat)
Mn	20	5	Respiratory System, CNS, Kidney	-	Affects central nervous system	+	-	0.21 g/kg (mouse)
Mo	9	0.35	Liver, Blood, Kidney, Bone	-	-	+	Death before weaning	0.19 g/kg (rat)
Ni	<10	0.45	Respiratory System, CNS, Skin	Various cancers due to nickel carbonyl	Respiratory disorders, Dermatitis	-	Death before weaning, runting	0.8 g/kg (dog)
Pb	120	0.3	G.I. Tract, CNS, Blood, Kidney,	-	Hemolytic and renal poison	-	Failure to reproduce	0.15 g/kg (rat)
Rb	1200	10	-	-	Disruption of cell membrane potential	-	-	1.21 g/kg (mouse)
Sb	<90	-	G.I. Tract, Respiratory System, CVS, Liver, Skin	-	Implicated in Heart Disease	-	-	0.6 g/kg (mouse)
Se	-	-	-	-	-	-	-	4.0 g/kg (mouse)
Se	15	0.06-0.15	G.I. Tract, CNS, Liver, Skin	Cancer of liver	Degeneration of liver and kidney, pneumonia	+	Teratogenic, death before weaning, runting	0.003 g/kg (rat)
Sn	30	17	G.I. Tract, CNS	-	-	-	-	0.16 g/kg (dog)
Sr	140	2	CNS, Teeth, Bone	-	-	+	-	0.4 g/kg (mouse)
Te	-	0.6	CNS, Liver, Kidney	-	Kidney and Liver Degeneration	-	Hydrocephalus	0.002 g/kg (rat)
Tl	-	-	G.I. Tract, Respiratory Tract, CNS, Liver, Kidney, Blood, Bone	-	Cumulative Hemolytic Poison	-	-	0.026 g/kg (rat)
U	0.02	-	Kidney	-	Kidney disease	-	-	-
V	30	2.5	Respiratory System, CNS, Skin, Kidney	-	-	+	-	0.2 g/kg (rabbit)
W	-	-	Bone	-	-	-	-	0.24 g/kg (rat)
Zn	2300	12	G.I. Tract, Skin, Bone	-	-	+	Mild Teratogenic effects, increased hydrocephalus	2.0 g/kg (rabbit)

G.I. - Gastrointestinal Tract
CNS - Central Nervous System
CVS - Cardiovascular System

TABLE 3

TRACE METALS IN COAL AND FLY ASH
(References 1-3, 6-10, 17)

Element	Average Concen. in Coal ($\mu\text{g/g}$)	Concen. Range in Coal ($\mu\text{g/g}$)	Concen. Remaining in Fly Ash ($\mu\text{g/g}$)	% Remaining in Fly Ash after Combustion at 500°C
Ag	-	0.1-2	0.4-3	790
As	5	0.5-93	2.8-200	35-50
B	55	5-224	-	795
Ba	64	2-500	110-700	-
Be	2	0.2-4	1-7	82
Cd	-	0.1-65	2-100	38
Co	12	1-43	25-70	790
Cr	20	4-54	80-500	795
Cu	12	5-61	33-300	795
F	-	25-220	10-100	-
Fe	-	1800-8000	-	790
Ge	8	1-43	-	795
Hg	2	0.2-5	0.1-18	0-10
In	0.18	-	0.2	-
Mn	30	6-181	150-500	795
Mo	6	1-30	34	67
Ni	20	3-80	45-300	76
Pb	9	4-218	95-440	37
Ra	-	-	-	-
Rb	25	-	180	790
Sb	-	0.2-8.9	5.6-100	50
Sc	8	-	29.5	790
Se	3	0.45-7.7	0.77-40	24
Sn	2	1-51	1.9-100	795
Sr	85	46-160	69-1000	-
Te	0.5	-	-	36
Th	3.47	-	17.1	790
Tl	0.125	<0.2-0.7	5-76	-
U	-	10-160	-	-
V	33	11-78	180-2000	70
W	0.93	-	2.7	790
Zn	329	6-5350	70-1000	795

TABLE 4

AMOUNTS OF SOME ELEMENTS RELEASED INTO THE ATMOSPHERE AS A
RESULT OF THE COMBUSTION OF COAL, OIL, WEATHERING PROCESSES
AND MINING IN 1967

(References 3, 18)

Element	Coal	Oil	Weathering		Mining $\times 10^6$ (kg/y)
	Combustion $\times 10^6$ (kg/y)	Combustion $\times 10^6$ (kg/y)	Mobilization $\times 10^6$ River Flow	(kg/y) Sediments	
Ag	0.07	0.00002	11	0.03	-
Al	1,400	0.08	14,000	140,000	-
As	0.07	0.002	72	-	2.7
B	10.5	0.0003	360	-	100
Ba	70	0.02	360	500	-
Be	0.41	0.00006	-	5.6	0.28
Bi	0.75	-	-	0.6	-
Cd	-	0.002	-	0.5	30
Co	0.7	0.03	7.2	8	15
Cr	1.4	0.05	36	200	2,000
Cu	2.1	0.023	250	80	4,000
Fe	1,400	0.41	24,000	100,000	-
Ga	1	0.002	3	30	-
Ge	0.7	0.0002	-	12	-
Hg	.0007	1.6	2.5	1.0	-
Mn	7	0.02	250	2,000	6,000
Mo	0.7	1.6	36	28	30
Ni	2.1	1.6	11	160	300
Pb	3.5	0.05	110	21	-
Rb	14	-	36	600	-
Sc	0.7	0.0002	0.14	10	-
Se	0.42	0.03	7.2	-	0.9
Sn	0.28	0.002	-	11	-
Sr	70	0.02	1,800	600	48
Ti	70	0.02	108	9,000	-
U	0.14	0.001	11	8	-
V	3.5	8.2	32	280	8
Zn	7	0.04	720	80	3,000

TABLE 5

ROUGH ESTIMATE OF AIRBORNE TRACE ELEMENTS RELEASED
FROM COAL FIRED POWER PLANTS IN 1970
(Reference 7)

Element	Concen. in Coal Used for Estimate ($\mu\text{g/g}$)	Stack Emission		
		Total, Coal- Fired Plants, Element Basis (tons/y)	Per 10^6 Btu in Coal (lb)	Per m^3 of flue gas (STP) (mg)
As	5	800	2.3×10^{-4}	0.2
B	55	1,600	4.4×10^{-4}	0.53
Ba	64	1,900	5×10^{-4}	0.6
Be	2	100	3×10^{-5}	0.04
Co	12	360	10^{-4}	0.12
Cr	20	600	1.6×10^{-4}	0.2
Cu	12	360	10^{-4}	0.12
Ga	5	150	4×10^{-5}	0.05
Ge	8	240	6.4×10^{-5}	0.08
Hg	2	600	1.6×10^{-4}	0.2
Mn	30	900	2.4×10^{-4}	0.3
Mo	6	180	5×10^{-5}	0.06
Ni	20	600	1.6×10^{-4}	0.2
Pb	9	270	7×10^{-5}	0.09
Rb	25	750	2×10^{-4}	0.25
Sc	8	240	6.4×10^{-5}	0.08
Se	3	90	3×10^{-5}	0.03
Sn	2	60	1.6×10^{-5}	0.02
Sr	85	2,500	7×10^{-4}	0.8
Ti	400	12,000	3×10^{-3}	4
V	33	1,000	2.6×10^{-4}	0.33
Zn	40	1,200	3×10^{-4}	0.4
Zr	76	2,300	6×10^{-4}	0.77

TABLE 6

TRACE ELEMENT CONTENT OF SOME CRUSTAL MATERIALS
(References 29,30)

Element	Average Concen. Igneous Rock ($\mu\text{g/g}$)	Average Concen. Shales ($\mu\text{g/g}$)	Average Concen. Sand Stones ($\mu\text{g/g}$)	Average Concen. Soils ($\mu\text{g/g}$)	Concen. Range Soils ($\mu\text{g/g}$)
Ag	0.07	0.05	0.05	0.1	0.01-5
As	1.8	13.0	1.0	6.0	0.1 -40
Ba	425.0	580.0	50.0	500.0	-
Be	2.8	3.0	<1.0	6.0	0.1 -40
Bi	0.17	1.0	0.3	-	0.1 -1.0
Cd	0.2	0.3	0.03	0.06	0.01-0.7
Co	-	-	-	1.4	-
Cr	100.	90.	35.	40.	7-300
Cu	-	-	-	20.	2-100
Ga	15.	19.	12.	30.	0.4 -300
Ge	5.4	1.6	0.8	1.0	1-5
Hg	0.08	0.4	0.03	0.3	0.01-0.8
Mn	-	-	-	850.	100-4000
Mo	-	-	-	2.	0.2 -5
Ni	75.	68.	2.0	40.	10-1000
Pb	12.5	20.	7.	10.	2-200
Rb	90.	140.	60.	100.	-
Sb	0.2	1.5	0.05	6.0	2-10
Sc	22.	13.	1.0	7.0	-
Se	0.05	0.6	0.05	0.2	0.01-2
Sn	2.	6.	0.5	10.	2-200
Sr	375.	300.	20.	300.	-
Te	0.001	-	-	10.1	0.5 -1.0
Ti	5700.	4600.	1500.	5000.	-
Tl	0.45	1.4	0.82	5.	-
V	135.	130.	20.	100.	20-500
Zn	-	-	-	50.	10-300
Zr	165.	160.	220.	300.	-

TABLE 7

DISTRIBUTION OF TRACE METALS IN SEAWATER
AND FRESHWATER

(References 31-33)

Element	Average Conc. Seawater ($\mu\text{g}/\ell$)	Average Conc. Freshwater ($\mu\text{g}/\ell$)
Ag	0.3	2.6
As	3.	6.4
B	4500.	100.
Ba	30.	43.
Be	0.01	0.19
Cd	0.1	9.5
Co	0.1	17.
Cr	0.05	9.7
Cu	3.	15.
F	1300.	90.
Fe	100.	52.
Ga	0.03	1.
Ge	0.07	-
Hg	0.03	0.08
In	-	-
Mn	2.	58.
Mo	10.	68.
Ni	2.	19.
Pb	5.	23.
Ra	6×10^{-8}	3.9×10^{-7}
Rb	120.	1.5
Sb	300.	-
Sc	0.004	-
Se	16.	20.
Sn	3.	0.04
Sr	8100.	217.
Te	-	-
Th	0.05	0.02
Tl	0.001	-
U	3.	1.
V	2.	40.
W	0.1	-
Zn	10.	64.

TABLE 8

AVERAGE TRACE ELEMENT CONCENTRATION IN PLANTS
(References 2,18,30)

Element	Average Soil Concen. ($\mu\text{g/g}$)	Concen. in Plants - dry weight ($\mu\text{g/g}$)	Annual Uptake by Grasses and Crops (Worldwide) (kg)	Concen. Toxic to Plants ($\mu\text{g/g}$)
Ag	0.1	0.06-1.4	-	-
As	6.0	0.2	10^7	2-1200
B	-	-	10^8	30-71000
Be	6.0	0.1	-	-
Bi	0.1-1.0	0.06	10^6	-
Br	-	-	10^8	-
Cd	0.06	0.06	10^7	10-20
Co	1.4	0.05-0.25	10^6	-
Cr	40	0.23	10^7	-
Cu	20	14	10^8	30
F	-	-	10^8	7.70
Ga	30	0.06	-	-
Ge	1.0	0.15	-	-
Hg	0.3	0.015	-	-
Mn	850	630	10^9	400
Mo	2	0.9	10^7	-
Ni	40	3	10^7	50
Pb	10	2.7	10^7	30
Sb	6.0	0.06	-	-
Se	0.2	0.2	10^7	-
Sn	10	<0.3	-	-
Sr	300	-	10^8	-
Te	10.1	-	-	-
Tl	5	-	-	-
Th	5	-	-	-
Ra	-	10-9	-	-
V	100	1.6	10^7	2.5
W	1	0.07	-	-
Zn	50	100	10^9	400

TABLE 9

CONCENTRATIONS OF TRACE ELEMENTS IN MAJOR FOOD CLASSES ($\mu\text{g/g}$)

(References 2,29)

Element	Sea Foods	Cereals and Grains	Fruits	Vegetables	Meats	Dairy Products	Nuts
As	1.5 -15.3	N.D.-2.4	N.D.-0.17	N.D.-1.3	N.D.-1.4	N.D.-0.23	-
Cd	0.05-3.66	0.01-0.57	N.D.-0.03	0.01-0.45	0.19-3.49	0.1 -0.56	0.03-0.07
Cr	N.D.-0.44	N.D.-0.52	N.D.-0.2	N.D.-3.62	0.03-0.27	-	-
Ge	0.12-3.63	N.D.-1.05	N.D.-0.85	N.D.-1.07	0.15-0.75	0.3 -1.51	N.D.-1.23
Ni	0.02-1.7	N.D.-6.45	N.D.-0.34	N.D.-2.59	N.D.-4.5	N.D.-0.03	-
Pb	0.15-2.50	N.D.-7.49	0.03-0.38	N.D.-1.26	N.D.-0.57	N.D.-0.79	-
Se	0.12-2.02	0.02-1.11	N.D.	N.D.-0.57	0.19-4.17	0.06-1.46	N.D.-1.03
Sn	0.49-4.30	N.D.-2.63	-	N.D.-9.07	0.32-3.44	0.19-0.96	-
Ti	0.02-0.88	N.D.-0.99	N.D.-0.38	N.D.-2.42	0.01-0.76	N.D.	-
Te	N.D.-0.78	N.D.-2.93	-	N.D.-0.77	N.D.	N.D.-2.39	N.D.-1.09
V	N.D.-5.1	N.D.-6.03	N.D.-0.18	N.D.-6.0	N.D.	-	N.D.-1.96

N.D. - Not detectable

TABLE 10

TRACE METAL CONCENTRATION FACTORS FOR MARINE AND
FRESHWATER FISH AND INVERTEBRATES

(Reference 34)

Element	Conc. Factor Freshwater Fish	Conc. Factor Marine Fish	Conc. Factor Freshwater Invertebrates	Conc. Factor Marine Invertebrates
Ag	2	3,330	769	3,330
As	333	330	333	333
B	0.2	-	-	-
Ba	4	-	-	-
Be	2	200	10	200
Cd	200	3,000	2,000	250,000
Co	320	100	200	1,000
Cr	4,000	3,000	20	2,000
Cu	200	667	1,000	1,670
F	-	-	-	-
Fe	-	-	-	-
Ge	3,300	3,300	33	15,700
Hg	1,000	1,670	100,000	33,300
In	-	-	-	-
Mn	660	660	40,000	10,000
Mo	10	10	10	10
Ni	100	100	100	250
Pb	300	300	100	1,000
Ra	50	50	250	100
Rb	2,000	-	-	-
Sb	1	40	10	5
Sc	-	-	-	-
Se	167	4,000	167	1,000
Sn	3,000	3,000	1,000	1,000
Sr	-	-	-	-
Te	400	-	75	100,000
Th	30	10,000	500	2,000
Tl	100,000	10,000	15,000	15,000
U	10	-	-	-
V	10	10	3,000	50
W	1,200	30	10	30
Zn	8,500	2,000	10,000	100,000

TABLE 11

CLASSIFICATION OF SOME TRACE ELEMENTS ACCORDING
TO THEIR TOXICITY TO MAMMALS INCLUDING
MAN AND AQUATIC ORGANISMS

(Reference 35)

Non Toxic	Very Toxic and Accessible	Toxic, but Rare or very Insoluble
Li	Ag	Ba
Rb	As	Ga
Sr	Be	Ti
	Bi	W
	Cd	
	Co	
	Cr	
	Cu	
	F	
	Hg	
	Ni	
	Pb	
	Sh	
	Se	
	Sn	
	Te	
	Tl	
	Zn	