

COURSE CODE:	EMT 305
COURSE TITLE:	Metals and the Environment
NUMBER OF UNITS:	2 Units
COURSE DURATION:	2 hours per week

COURSE DETAILS:

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Other Lecturers:	

COURSE CONTENT:

Origin of Metals, Classification of metals, Utilization of metals in industries, Sources of metal pollution, geological weathering, industrial discharge, metals fabricating and furnishing, leaching of metals from garbage, agricultural waste products. Effect of metals on the environment, sediment, water, air and food. Adverse effect of heavy metals – poisoning effect of Pb, Cd, Zn and Hg . Other effect, e.g. neurologic, and renal effect. Analysis of metals in environmental samples.

COURSE REQUIREMENTS:

This is a compulsory course for all 300 level students in the EMT Department. It is compulsory that students should participate in all the course activities and have minimum of 75% attendance in order to be qualify to write the final examination.

READING LIST:

1. Walker, B.W. Jr. 1992; Perspective on Quantitative Risk Assessment; Journal on Environmental Health 35 (1); 15 – 20
2. Amdes, M doull. J. and Khases C.D. eds 1991. Casasset & Doulls Toxicology: The Basic Science of Poisons 4thed. Tarry town N.Y. Pergamon
3. Carson, R. 1962. A classic book on problems associated with toxins in the environment.

LECTURE NOTES

EMT 305 (METALS AND ENVIRONMENT)

OCCURRENCE OF METAL

Metals occur naturally in the environment but due to industrial revolution via technological advancement, metals concentrations in the environment are becoming increasingly high.

Elevated metals concentration in ecosystem occurs in areas such as:

1. Urban areas i.e. cities
2. Metalliciferous mines where metals are being mined
3. Major roads systems vehicle emissions
4. Areas characterized by auto mobile activities e.g. mechanic workshop

Metals occurrence in the environment has become an environmental concern because the globe is said to be experiencing a silent epidemic of environmental poisoning, from the ever increasing amounts of metals released into the biosphere.

Indicators of environmental metal pollution

1. Soil
2. Stream
3. River
4. Groundwater
5. Sediment
6. Benthic organism (crab)
7. Vegetation sample (plant sample)
8. Geochemical sample
9. Air

METAL IN SOIL:

Soils are dynamic bodies in equilibrium with environmental forces acting on them. A wide variety of factors influence metal translocation from the root to the shoot.

In scientific experiments, the uptake of metals from soil is greater in plants growth in pots of soil in the greenhouse/screenhouse than from the same soil in the field due to the fact that:

1. Differences in micro climate and soil moisture
2. Roots of container-grown plants growing solely in contaminated soil while those in the field-grown plants may reach down to less contaminated soil.

METAL PHYTOTOXICITY:

Elevated or excess concentration of both essential and non-essential metal result in phytotoxicity via mechanism such as:

1. Changes in the permeability of the cell membrane
2. Reaction of sulphhydryl (SH) GROUPS
3. Competition for sites with essential metabolites
4. Affinity for reactions with phosphate groups and active groups of ADP or ATP
5. Replacement of essential ions especially cations
6. Occupation of sites for essential groups such as phosphate and nitrate

Often, plant can accumulate high amount of metals in their tissue without any obvious sign of these. Food plants which tolerate relatively high concentration of these potential hazardous metals are likely to create a greater health risk than those which are more sensitive and show definite symptoms of toxicity.

Plant tolerance mechanism to metal toxicity

Various mechanisms include:

1. Selective uptake of ions
2. Decreased permeability of membranes or other differences in the structure and function of membranes
3. Immobilization of ions in root, seeds etc

4. Removal of ions from metabolism by deposition (storage) in fixed and/or insoluble forms
5. Alteration in metabolic pattern i.e. increased enzyme system that is inhibited or increased antagonistic metabolite or reduced metabolic pathway by-passing an inhibited site.
6. Adaptation to toxic metal replacement of a physiological metal in an enzyme

METALS IN AQUATIC ENVIRONMENT

1. High temperature increases the solubility of metals
2. Metals precipitate in hard water (clump together)
3. Metals are less soluble in salt
4. Metals are most soluble in acidic water
5. Metals that are not dissolved in water column collect in the river sediments and organic debris
6. The organism (biota) in the water system take up the metal pollution from water, organic matter or sediments via eating or respiration
7. Benthic organism and their predator usually accumulates these metals, which could lead to biomagnifications (via food chain and the concentration of the toxins increases in the organism of higher tropic levels.

Metal excluders: These plants prevent metals from entering their aerial parts or maintain low and constant metal concentration over a broad range of metal concentration in soil. They mainly restrict metal in their roots. This is possible because the plant may alter its membrane permeability, change metal binding capacity of cell walls or exclude more chelating substances.

Metal indicators: These plants specie are sensitive to metal concentration in the environment. Obvious sign of phytotoxicity manifest easily in them.

Metal accumulators: These plants can take up and accumulate metal in their tissue (aerial part) to some extent without manifesting phytotoxicity.

Hyper accumulators: They accumulate in high percentage of metal in their tissue (aerial parts). The metals can be concentrated either in their roots, shoots, and/or leaves. They tolerate high metal level by producing intracellular metal binding compounds (chelators) or alter metal compartmentalization pattern by storing metals in non-sensitive parts.

Hyper accumulators are suitable for phytoremediation purposes which is the use of plant for the cleaning of contaminated environment. The use of plant to clean metal contaminated soils is known phytoextraction but if it is water, it is called rhizofiltration.

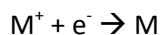
INTRODUCTION TO METALS

Metals are characterized by several distinctive properties such as high electrical conductivities, metallic luster, malleability and ductility. Non-metal does not usually exhibit such behavior. Nonetheless, the borderline between the two classes of elements (metals and non-metals) are not very rigid as there are some exception. The best distinguishing feature between metals and non-metals lies in the nature of their oxide. Metals form predominantly basic oxides whereas non-metal form acidic oxides but there could be some exception.

Types of metals

The alkali metals

Alkali metals are lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs). These metals are very reactive and electropositive (they very easily loose electron:



The alkaline earth metals

Alkaline earth metals are beryllium (Be) magnesium (mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra). Be differs in chemistry from the rest as it shows a considerable degree of covalent character. Radium is very radioactive. Alkaline earth metals are highly reactive.

Metalloids

Metalloids are the elements found along the stair-step line that distinguishes metals from non-metals.

This line is drawn from between boron and aluminum to the boarder line between polonium and astatine. The metalloids are boron, silicon, germanium, arsenic, antimony, tellurium, and polonium. Though aluminum falls in the group of elements along the stair-step line in the periodic table, it is a metal, not a metalloid. Metalloids have properties of both metals and non-metals. Some of the metalloids such as silicon and germanium are semi-conductors, meaning that they can carry electrical charge under some special condition. This property makes metalloid useful in computers and calculators.

Macro-nutrient elements

These elements needed in trace amount, not very soluble in water and toxic in high concentration. Examples include cobalt (Co), copper (Cu), zinc (Zn) and iron (Fe).

Heavy metals

Those metals described as heavy metals are those, which in their standard state have specific gravity (density) of more than 5g/cm^3 . it is not every heavy metal that is harmful to life. For instance, copper (Cu), nickel (Ni), chromium (Cr) and iron (Fe) are heavy metals which are essential to life. Some heavy metal such as cadmium (Cd), lead (Pb), silver (Ag) and mercury (Hg) are highly toxic and not water soluble. Heavy metals include micronutrient elements, toxic metals and precious metal such as platinum, silver and gold.

Increasing industrialization has been accompanied throughout the world by extraction and distribution of metal from their natural deposits. The possible general route and interchange of metal pollutants in the environment are illustrated in Figures 1 and 2. as a result of anthropogenic activities, metals a now wide spread in the environment. There is interchange of metals among the different segments of the environment. Civil and industrial activities of man result in various wastes, which could be finely dispersed and/or in solutions, by way of effluents, sewage, dumps and dust. Metals contained in them are thus released into the water, soil or air and thus into food chain. Not all traces of heavy metals are as a result of anthropogenic activities. Metals occur naturally, hence, even foodstuffs produced in completely unpolluted areas are not entirely free of heavy metals. As a result, there is need for preparation of standards for heavy metals in foodstuffs, water among others.

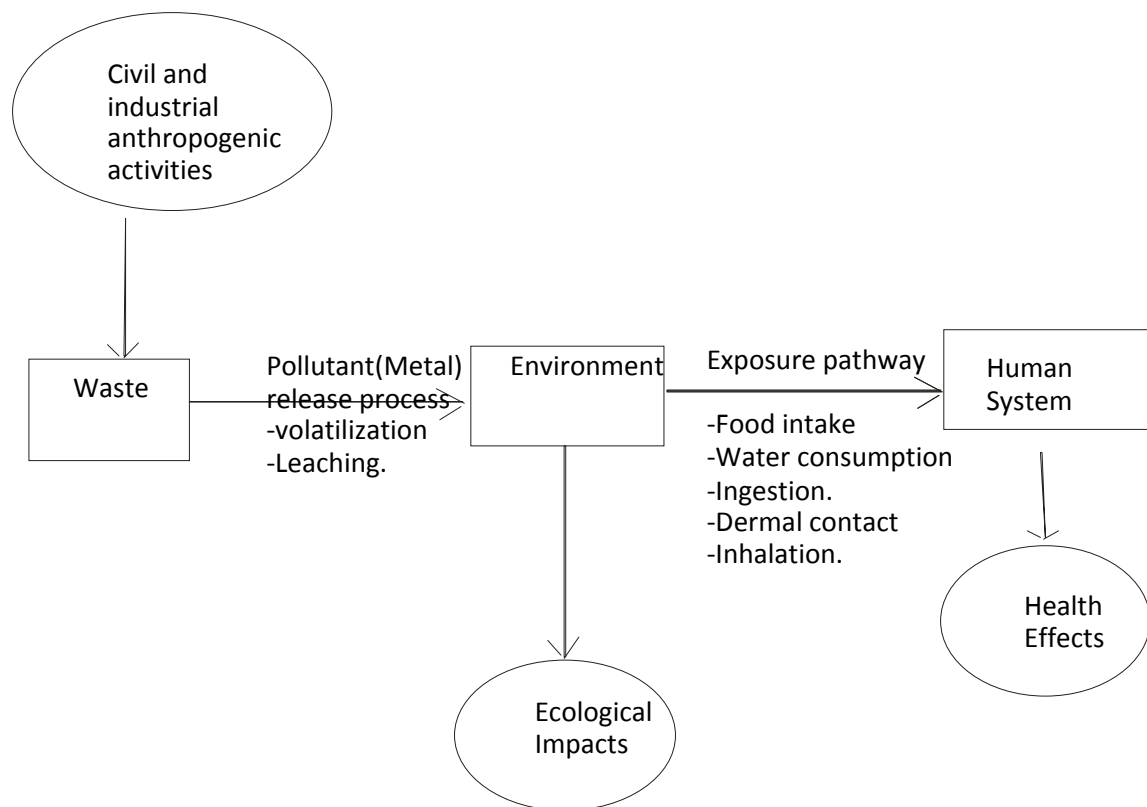


Fig.1: Relationship between metal generation, exposure pathway and environmental impact.

FATE OF METAL POLLUTANTS IN THE ENVIRONMENT

The fate of metals in the environment is complex. It depends on factors like pH, hardness, temperature, salinity, presence of competing ions and organic matter contents either in the aquatic or terrestrial environment. Soil texture, electrical conductivity and cation exchange capacity (CEC) are added factors in terrestrial environment.

In the aquatic environment, the general rules include;

1. High temperature increase the solubility of metals
2. Metals precipitate in hard water (clump together)
3. Metals are less soluble in salt water
4. Metals are most soluble in acidic water

Metals that are not dissolved in water column collect in the river sediments and organic debris. The organisms (biota) in the river system take up the metal pollutants from water, organic matter and/or sediments via eating or respiration. The uptake of metals by biota also varies with environmental condition.

Benthic organism and their predator usually accumulate these metals, which could lead to biomagnification. Biomagnification means that an organism and its predator accumulate a toxin via food chain and the concentration of the toxins increases in organism of higher trophic levels.

METAL POLLUTION

The deposition of metals from the atmosphere and accumulation of these elements in the terrestrial ecosystems have become a global issue because small amounts of certain metals can damage various organisms. Metal pollution is dangerous to the health of all life forms including humans.

Health effects;

Diseases and health problem associated with heavy metal poisoning include cardiovascular problems (cardiovascular problems are associated with blood vessel damage, hypertension, decreased red blood cell count, peripheral vascular diseases, cardiovascular disease), renal (cancer of the colon, pancreatic, stomach and rectal), hepatic impairment (liver and kidney impairment), respiratory system issues (respiratory tract cancers, asthmatic condition, pneumonia, pulmonary edema and pulmonary fibrosis), reproductive problems (these include genital abnormalities, menstrual pains, birth defect, immune system deficiencies, immuno-suppression, inhibition of lymphocytes, decreased white blood cell count).

Other problems associated with metal pollution are hair loss (alopecia), skin disorder (rashes, dermatitis, eczema, irritated skin, cogitative impairment (dementia and impaired reaction time etc, mental impairment, poor memory, difficulty in understanding abstract ideas or carrying out complex commands), nervous system (loss of feeling an numbness in extremities), physiological impairment (nerve conductivity, spinal cord, abnormal EEG's etc), motor disorders (difficulty in walking, talking and swallowing, jerks, loss of balance, problems with sitting or lying and seizure etc), sensory abnormalities (abnormal sensations in the mouth and extremities, hearing loss, diminished touch sensations, blurred vision and sensitivity to light).

Metal pollution is also associated with physical disturbances (decreased muscular strength, headache, colic), speech problems (comprehension deficit, slurred speech, loss of speech or development problems with language, speech comprehensive deficit, articulation problems, slurred speech and unintelligible speech), psychiatric disturbance (social withdrawal, stereotyped behavior, depression and mood swings, schizoid tendencies, aggressive behavior, suicidal behavior, sleep difficulties, chronic fatigue, weakness, malaise, eating disorders, anxiety and nervous tendencies) eye contact problems (impaired visual fixations).

METAL TOXICOLOGY

Metal toxicology is classified into two basic types acute and chronic toxicity. Acute toxicity is the short term effect of metal exposure to an organism within a period of up to 96hrs. Chronic toxicity is long term effects often due to cumulative exposure. There are symptoms for the two types of toxicities. Acute and chronic toxicities vary with metal type and for a particular metal the chemical forms contributed significantly.

Factors influencing metal toxicology

1. Metal metabolism:

The metabolism of a toxic may be related to an essential element. For instance, Pb and Ca (central nervous system and bone: Fe and Zn (heme). A decreased in dietary calcium, for instance, will influence toxicity of metals such as Pb and Cd. Metabolically related essential element may alter toxicity by interaction at the cellular level.

2. Metal-protein complexes:

Many toxic metals form complexes with enzymes thereby inhibiting the biochemical function of these enzymes. The protein complexes include Pb, Hg and Fe.

3. Speciation:

Metal speciation is synonymous to chemical forms of metals indicated by their oxidation state. It is important for pulmonary and gastro-intestinal absorption as well as body distribution. It affects the solubility of the metal.

4. Exogenous factors:

These include age, diet, weight, body mass index and interactions concurrent exposure with toxic metals. Susceptible population such as pregnant women, developing fetus, young children, aged, individual with communicable diseases like tuberculosis and HIV/AIDS and/or those affected by chronic illness are also included. Populations living in poor socio economic conditions that are prevalent in the developing countries are at

risk. The immune status of an individual is an additional toxicological variable for metals that produce hypersensitivity reactions (the lower the immunity, the greater the risk).

5. Dietary factors:

The effects of dietary factors are mostly at the level of absorption from gastro-intestinal tract. Vitamin C reduces Pb and Cd absorption. There is inverse relationship between protein content of diet and some metal (e.g. Cd and Pb) toxicities.

6. Life-style:

Habits such as smoking or alcohol consumption mostly have indirect influences on toxicity. Cigarette smoke contains some toxic metals such as Cd and Pb. Cigarette smoking may influence pulmonary effects. Alcohol consumption may influence toxicity by altering diet and reducing essential mineral intake.

LEAD AND THE ENVIRONMENT

Chemistry of lead

Lead as a metal denoted by the symbol Pb. Its atomic number is 82, atomic weight is 207.2g/mol and it is a p-block element. In its standard state (298K), Pb is bluish-white in color. It is very soft, highly malleable, ductile and a relatively poor conductor of electricity. It melts at 327°C and its boiling point is 1750°C. Lead has low water solubility, is very resistant to corrosion but tarnishes upon exposure to air.

Lead has the most stable divalent (+2) oxidation state though it also occurs in tetravalent (+4) oxidation state. Lead in +2 oxidation state (Pb^{2+}) has the tendency to form strong bonds with groups containing nitrogen and sulphur (e.g. CN^- , RS^- , SH^- and imidazoles) in biological systems.

OCCURRENCE OF LEAD

Lead occurs naturally in the earth crust, usually in ores such as:

- Galena (PbS) (major ore)
- Cerrusite ($PbCO_3$)
- Anglesite ($PbSO_4$)
- Lanarkite ($PbO \cdot PbSO_4$)
- Leadhillite

Uses of lead

Lead is valuable in many industrial applications. It is useful in food and medical formulations and preparation, cosmetics, arms, ceramics, batteries, radiators of cars and trucks. Some jewelries, pipes, inks and pencils also contain the metal.

Environmental study of lead

Lead is a highly toxic trace element with no recognized biological requirement in organisms. Moreover, there may be no concentration threshold for Pb in humans or other mammals. The concentration of the metal has been substantially elevated by industrial release, sequel to anthropogenic activities; the relative environmental Pb contamination is

unparalleled among the elements and most of it dispersed as an environmental pollutant on a global scale. Pb is therefore very ubiquitous (found in several places), being found in the atmosphere, soil, water, plant, foods and sediments.

Lead in air:

Approximately 94% of the Pb in the atmosphere is derived from anthropogenic sources with a higher proportion in urban areas where there is heavy motor traffic. The increase in aerial dispersion from anthropogenic emission has increased the atmospheric flux, leading to higher levels of Pb in rivers, seas and on vegetation and soils.

Lead in soil:

Lead gets onto soil through paint, dry and wet depositions from the atmosphere and industrial contamination (effluents and solid discharges). Lead exhibits long residence time, sparingly soluble as a result of rapid conversion to $\text{Pb}(\text{SO}_4)$ at the soil surface and it forms relatively stable organo-metal complexes or chelates with organic matter in soil. In soil with pH of more than 5.0 and at least 5% organic matter, atmospheric Pb is retained in the upper 2 to 5cm of undisturbed soil.

Lead in water:

Lead has the tendency to form compounds of low solubility with major anions found in natural water. Some of them are found in an undissolved form (colloidal particles or larger undissolved particles of PbCO_3 , PbO and $\text{Pb}(\text{OH})_2$). The ratio of Pb in suspended solids to Pb in dissolved form has been found to increase from 4:1 to 27:1 in urban streams, implying increased pollution. Consumption of such untreated water may lead to Pb poisoning.

Occupational exposure to lead

Occupational exposure to lead occurs when one is exposed to some doses of the metal at work place. The following groups of people are susceptible:

- Plumbers, pipe fitters
- Foundry workers
- Glass manufacture
- Printers/typesetters (not very common)
- Construction and demolition workers
- Petrol station attendants
- Police officers
- Traffic wardens
- Battery manufacturers
- Paint strippers
- Bridge construction workers
- Waste management personnel

Non-Occupational exposure to lead

This is a result of environmental exposure to the metal which does not emanate from work places. Examples include:

- Inhalation of Pb aerosols released into the atmosphere via anthropogenic activities such as waste combustion, vehicle emission, industrial emission.
- Consumption of contaminated water
- Direct dermal contact with Pb compounds, especially organic compounds
- Accidental ingestion of Pb compound
- Ingestion of contaminated soil and dust by children

- Exposure through hobbies and related activities such as target shooting at firing ranges, pottery glazing, tyre burning, bush burning, combustion of fossil fuels, indiscriminate solid waste combustion.
- Consumption of contaminated food.

Contaminated foods are a principal non-occupational exposure of Pb especially in countries or regions where the use of leaded gasoline has declined. It is found in foods such as root crops, nuts, cereals, beans, fruit, vegetables and water. About 50 to 99% of Pb in food is derived from direct and indirect atmospheric inputs while the rest is derived from soils (primary minerals, humic substances and soil moisture).

Leafy crops are most susceptible to contamination from atmospheric deposition of industrial Pb. These crops include green leafy vegetables (e.g. fluted pumpkins: *Telfairia occidentalis*, spinach, lettuce etc), wheat, rice, amongst others. Lead contamination in foods not directly exposed to atmospheric depositions are very much lower than those directly exposed. These include root crops, nuts, beans and some fruits.

Atmospheric industrial Pb is also the primary source of Pb contamination of livestock and poultry. This occurs initially through the ingestion of contaminated forage, feed and soils and subsequently during the processing of meat products. Dietary intake of dairy products also exposes man to Pb contamination. Atmospheric exposure of foods via improper packaging procedures enhances food Pb contamination especially such food sold in outdoor markets in regions where leaded gasoline usage has not been phased out. Indiscriminate open-air combustion of wastes releases lead into the atmosphere and subsequently unto exposed foods.

Toxic effect of lead

- Lead serves no useful purpose in the human system (body) and its presence in the body can lead to toxic effects, regardless of exposure pathway. Lead competes with Ca^{2+} for sites in cellular and sub-cellular systems. These include synatosomes, mitochondria, membrane vesicles, protein kinase C and other Ca^{2+} binding proteins. Hence the primary mechanism of Pb toxicity is associated with the alteration of calcium mediated cellular processes and mimicry of Ca^{2+} binding to regulatory proteins including those with sulfhydryl (SH), amine, phosphate and carboxyl groups. Factors that influence Pb toxicity are exposure time, exposure level (concentration) and other factors (see factors influencing metal toxicity).
- Lead is absorbed in the bloodstream (particularly true for inorganic Pb compounds), soft tissue, bones and teeth. A larger percent (about 90) of absorbed Pb gets to the bones and teeth and the rest are found in the soft tissue and blood. Organic forms of Pb are fat soluble, therefore has the tendency to distribute to the brain. Half lives for blood, soft tissue and bone are approximately 25days, 40days and 25years respectively.
- Lead accumulates over lifetime and is released very slowly. It builds up in the body leading to Pb poisoning.

Short-term exposure effect

Vomiting, diarrhea, convulsion, coma, constipation, irritability, include tiredness, irritability, muscle and joint pain, headache, stomach aches and cramps (lead colic).

Long-term exposure effect

Manifestations of Pb poisoning are neurological, hematological, renal, endocrine and reproductive.

Neurological

- Peripheral neuropathy and paralysis (late sign of Pb intoxication)
- Reduction in intelligence quotient in children, leading to poor school performance
- Lead associated hearing loss, especially of the high frequencies, contributing to learning disability
- Impaired concentration

Hematological

- Lead interferes with two enzymes necessary for haem-biosynthesis namely δ -amino laevulinic acid dehydratase (ALAD) and ferrochelatase. Ferrochelatase catalyses the incorporation of iron (Fe) into protoporphyrin. Increased erythrocyte protoporphyrin results from this inhibiting effect of lead. With prolonged elevation of blood lead levels, erythrocyte survival time decreases, resulting in anaemia.

Renal and endocrine

- Lead produces proximal tubular dysfunction
- It impairs the function of renal enzymes such as 2, 5-hydroxyvitamin D-1 α -hydroxylase, which converts 25-hydroxyvitamin D to the biologically active compound 1,25-dihydroxyvitamin D.
- Lead reduces the binding of follicle-stimulating hormone to receptors in the cells of the testes
- Lead crosses the placenta, producing urogenital, rectal and vertebral malformation in the fetus

Reproductive

- Declined fertility in men through sperm damage
- Miscarriages and subtle abortions

Others include behavioral disruption (aggression, impulsive behavior and hyper activity) and rise in blood pressure.

GUIDELINES FOR LEAD IN THE ENVIRONMENT

Body burden

The biological exposure index (BEI) is guidance for assessing biological monitoring results. Zero Pb level in the human body is desirable. However, this may not be practical because Pb is very much in the environment. Consequently, international bodies came up with guidelines.

1. Children blood Pb level should be below 10 μ g/dL
2. Biological exposure index (BEI) is 30 μ g/dL
3. Workplace air Pb is kept at 50 μ g/m³ averaged over an 8-hour workday for permissible exposure limit.

If a worker has $\geq 40\mu$ g/DI, a medical examination is recommended.

If a worker has up to 60 μ g/DI on three or more tests, the worker must be removed from exposure to Pb until the blood Pb level falls below 40 μ g/dL.

If the workplace air Pb level is 30 μ g/m³ for more than 30 days per year, there should be periodic monitoring of the blood Pb level for the workers to ensure safety.

Note: 1. 50 μ g/m³ = permissible exposure limit at workplace.

2. $30\mu\text{g}/\text{m}^3$ = action Pb level at workplace
3. The maximum contaminant level goal (MCLG) is Zero

Guideline for lead in soil, water, crops and foods have been established. These values are periodically reviewed and reduced in order to reduce Pb poisoning.

CHROMIUM AND THE ENVIRONMENT

Chemistry of chromium

Chromium is denoted by the symbol Cr. It is a lustrous, brittle hard metal. It is silver-gray in color and does not tarnish in air. Chromium is unstable to oxygen i.e. it reacts with oxygen to produce a thin oxide layer that is impermeable to oxygen and thus protects the metal below.

Chromium has atomic number 24, atomic mass $51.996\text{g}/\text{mol}$, electronegativity 1.6, density $7.19\text{g}/\text{cm}^3$, melting point and boiling point of 1907°C and 2672°C respectively.

Uses of chromium

Chromium was discovered by Wöhler in 1797. The metal is very useful in many areas of life. It has industrial application, medicinal usefulness and also useful in foods.

Industrial application of chromium

1. Alloys such as stainless steel
2. Chrome plating. (chrome is a hard shining metal used as a protective covering for other metals.)
3. Ceramics
4. Used to impart corrosion resistance and shiny surfaces in metallurgy
5. Dye manufacture
6. Pigment manufacture
7. Used in paint production
8. Chromium salts are used to impart colors to glass. E.g. emerald green color.
9. Miscellaneous uses.

Chromium in food and medicine

Trivalent chromium (Cr^{3+}) is essential for humans, together with insulin. It removes glucose from blood. This implies that chromium deficit may enhance diabetes. To this effect, chromium is used in food supplement formulation and also in the manufacture of medicines. It also plays an important role in fat metabolism.

Occurrence of chromium

Chromium occurs as ores. It is predominantly mined as chromate (FeCr_2O_4) ore. Chromium ores are mined in places like South Africa, Zimbabwe, Finland, India, Kazakhstan and Philippines. It is also found in Canada.

Chromium occurs naturally in many vegetables, fruits, meats, yeasts and grains.

Occupational exposure to chromium

People who work in the steel and textile industries and in workplaces where chromium salt are utilized are exposed to the fumes or direct dermal contact.

Non-occupational exposure to chromium

For most people eating foods that contain Cr^{3+} is the main route of chromium exposure/uptake, storage of food in tanks or cans may increase Cr^{3+} concentration. Anthropogenic activities may lead to the release of Cr into water, air and soil, resulting in non-occupational exposure.

Environmental effect of chromium

Chromium exists in the +3, +4, +5 and +6 oxidation state but the two predominant forms are the +3 and +6 states.

Chromium enters water and soil in the trivalent (+3) and hexavalent (+6) forms, through natural processes and anthropogenic (human activities).

Human activities that increase the concentration of Cr^{3+} in the environment are:

- Steel manufacturing
- Leather manufacturing
- Textile

The major anthropogenic activities that increase the concentration of Cr^{6+} in the environment are:

- Chemical industries
- Leather manufacturing
- Textile industries
- Electro-plating
- Metallurgical fabrication
- Other Cr^{6+} applications in industries.

The combustion of coal, waste materials containing Cr release the metal into the atmosphere and through waste disposal, chromium ends up in soil. Most of the chromium in air will eventually settle in soil and water.

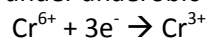
Chromium in soil strongly adheres or attaches to soil particles. This reduces the mobility of chromium in soil and thus reduces ground water pollution by the metal. In water, Cr absorbs into the sediments.

Increased chromium concentration in soil via anthropogenic activities can lead to higher chromium concentration in crops which gets to man via food chain. Soil acidification (reduced soil pH) enhance chromium crop uptake. Note that crops usually takes up Cr^{3+} from the soil. Cr^{3+} is an essential form of chromium but when concentrations exceed safety threshold or recommended value, negative effects will occur.

Chromium does not ordinarily accumulate in fish but high concentrations of the metal, due to the disposal of metal products in surface waters, can damage fish gills, especially for fishes that swim near the point of disposal.

Hexavalent chromium (Cr^{6+}) is very toxic to fauna and flora.

Note: 1. chromium (VI) compounds are stable under aerobic conditions but are reduced to chromium (iii) compounds under anaerobic conditions.



The reverse ($\text{Cr}^{3+} \rightarrow \text{Cr}^{6+} + 3\text{e}^-$) is a possibility under an oxidizing environment.

2. Chromium solubility in soil water is lower than the solubility of other potential toxic metals. This explains the relatively low crop uptake of the metal (Cr).

3. Chromium (VI) compounds are toxic to both plant and animals at very low concentrations. The toxicity is pH dependent. Cr^{6+} compounds are more mobile in soil than Cr^{3+} compounds, but Cr^{6+} are easily reduced to Cr^{3+} . Soluble chromate (Cr^{6+}) is converted to insoluble chromium (iii) salts and consequently plant availability of Cr^{6+} decreases. This mechanism protects the food chain from high amount of chromium.

Health effect of chromium

Exposure route:

People are exposed to chromium in these four basic ways:

- Breathing (inhalation)
- Eating of contaminated food)
- Drinking of contaminated water
- Skin contact (with chromium compounds/salts).

Note: The level of Cr in surface water, drinking water and air is generally low.

Contaminated ground water may contain the dangerous Cr^{6+} .

Health effects: Trivalent chromium (Cr^{3+})

Chromium (iii) is an essential nutrient to humans and its deficiency may cause diseases such as heart problems, diabetes and metabolic disorders. Yet when consumed in excess can be harmful. It can cause adverse health effect such as skin rashes. Chromium (iii) is not yet classified as carcinogenic according to International Agency for Research on Cancer (IARC).

Health effect: Hexavalent chromium (Cr^{6+})

Hexavalent chromium (Cr^{6+}) is a danger to human health, it is carcinogenic. The most dangerous compounds of Cr^{6+} are:

1. Calcium chromate
2. Chromium trioxide
3. Lead chromate
4. Strontium chromate
5. Zinc chromate

Health problem caused by chromium (VI) compounds are:

- Skin rashes
- Upset stomach and ulcers
- Respiratory problems
- Weakened immune systems
- Kidney and liver damage
- Alteration of genetic materials
- Lung cancer
- Death.

Apart from skin rashes, the adverse effects of Cr^{6+} compounds on the skin include ulceration, dermatitis and allergic reactions.

Inhalation of hexavalent chromium compounds can result in ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis and edema. It also causes nose bleeds.

Respiratory symptoms include:

- Coughing
- Sneezing
- Shortness of breath
- Nasal itch

Safety threshold:

1. Daily intake = 120µg (microgram)
Doses larger than 200µg are toxic.
2. The guideline for Cr in agricultural soils are approximately 100mg/kg.

MERCURY AND THE ENVIRONMENT

CHEMISTRY OF MERCURY

Elemental mercury (Hg) is a silver-white, heavy liquid at ambient temperature. It has atomic mass of 200.6 g/mol, boiling point of 356.7°C, melting point of -38.87°C, and vapor pressure of 0.3 pa at 25°C.

The prevalent oxidation (valence) states for mercury are the +1 (Hg⁺) and +2 (Hg²⁺) states. The predominant of the two states is the +2 state. Mercury forms a variety of organic and inorganic salts.

Examples of the inorganic salts are:

- Mercuric chloride (HgCl₂)
- Mercuric nitrate (Hg(NO₃)₂)
- Mercuric sulphide (HgS)
- Mercuric sulphate (HgSO₄)

The frequently encountered organic mercury salt is methyl mercury compound [Hg(CH₃)₂]. This compound is formed as a result of anaerobic microbial activity so is enhanced in environments characterized with high level of organic matter.

Occurrence of mercury

Mercury is found naturally in small amounts in rocks, soils and oceans. The most important ore of mercury is cinnabar (HgS), called mercury sulphide.

Uses of mercury:

Elemental mercury is an important industrial raw material, and the compounds could also be utilized.

Some of the industrial applications include:

- Industrial production of mercury-containing latex paint
- Electrolytic production of chlorine and caustic soda from brine (chlor-alkali industry)
- Production of amalgams for dentistry (tooth-filling materials)
- Production of preservatives
- Production of lubricating oil
- Production of pigments
- production of cosmetics e.g. facial mascard
- Useful in heat transfer technology
- Manufacture of gadgets such as electrical switching equipment, batteries, measuring and control equipment such as thermometers, barometers, manometers etc
- Manufacture of fungicides in agriculture, especially used for seed dressings.
- Useful in medicinal formulation such as diuretic, laxative and disinfectant, also in nasal sprays. It is used in diaper rash ointment for children and in eye drops etc.

Environmental exposure to mercury

Exposure route:

- Inhalation
- Ingestion
- Dermal contact

Occupational exposure to mercury

Population working in industries that utilizes mercury as earlier specified is prone to occupational exposure. Worker in such places come in contact with mercury in toxic form during:

- Transportation, handling and production of elemental mercury
- Lax safety measures during use and handling use and handling of mercury containing industrial production material.
- Excessive inhalation of mercury fumes during production process
- Prolonged use of mercury-containing gadgets such as electrical switches, barometers etc.

Non-occupational exposure to mercury

- This is exposure that occurs outside the workplace. The high vapor pressure of mercury encourages vaporization or volatilization. Hence, released of uncovered Hg can rapidly become an air hazard. Inhalation of such air introduces the metal to man.
- The filling of the teeth with Hg-amalgam can release the metal during normal chewing.
- Fish consumption: This constitutes the largest source on non-occupational exposure to the general population. Methyl mercury accumulates in fish body and bio-accumulates up the aquatic food web.
- Exposure to medicine that contains Hg such as laxatives and disinfectants etc.

HEALTH EFFECT OF MERCURY IN MAN

Acute health effects

This result from high exposures, symptoms of acute exposure via inhalation of Hg vapour are often cough, chest pain, chest tightness, difficulty in breathing and stomach upsets. If not properly handled, pneumonia may result and this could be fatal.

Acute exposure via ingestion (swallowing) of mercury compounds, especially inorganic salts, nausea, vomiting, diarrhea and severe kidney damage may occur.

Chronic health effect

This result from repeated exposures. Sometimes, high single dosage could result in chronic health effect. Some of these effects include:

1. Gum problems: Soft and spongy gums, loose teeth, sore development and possibilities of increased saliva
2. Mood and mental changes: Wide range of mood changes. People suffering from chronic Hg poisoning often have mood swings. They could be irritable, frightened, depressed or excited for no obvious reason. They are extremely upset when criticized, loose self confidence etc. they also suffer memory loss and often hallucinate. Such people could loose the ability to concentrate
3. Nervous system: Muscular tremor such as shaking and tremor of the tongue and eyelids. Eventually, there may be lack of balance especially when walking.
4. Skin : Rashes, allergy and burns
5. Reproductive system: Birth defects, damage to the unborn child who may develop problems with vision, smelling, hearing, memory and mental ability.
6. Eye: Irritation, discoloration
7. Brain damage: The brain is a target organ for both ionic and organic mercury. Elemental Hg has high lipid solubility, so when inhaled, about 75 to 85% is rapidly absorbed across the lungs and into the blood stream. A portion is converted to divalent mercury (Hg^{2+}) in the red blood cells, while the remaining portion is directly transported to the brain unchanged. It readily cross the blood-brain barrier, oxidized to ionic mercury in the brain. Elemental mercury and methyl mercury causes neurotoxicity with symptoms such as:
 - Tremors affecting the hand that may progress to the other parts of the body.
 - Numbness of fingers and toes
 - Slurred speech

- Erethism (emotional disability: irritability, extreme nervousness, shyness and loss of confidence)
 - Fatigue, insomnia, hallucination, visual loss and hearing loss.
8. Central nervous system: Micromercurialism or asthemic-vegetative syndrome occurs. This is a non-specific condition of the central nervous system (CNS), characterized by the following symptom:
- Tremor in fingers, eyelids, lips
 - Enlarged thyroid
 - Increased radio-iodine uptake by the thyroid
 - Labile pulse
 - Increased mercury excretion in urine
 - Hematological changes etc.
 - Increased emotional excitability (erethism)
 - Memory loss, hallucination, depression etc (emotional changes)
9. Kidney damage: The kidney just like the brain is also a primary target organ for both elemental and ionic mercury. The mechanism of toxicity is associated to the binding of mercury to important or key enzymes and structural proteins. Exposure of Hg to the kidney may cause:
- Tubular proteinuria (Hg in urine)
 - Tubular necrosis
 - Tubular-interstitial nephritis
 - Tubular calcification
 - Glomerular nephritis
10. Cardiovascular system effects: Accumulation of both organic e.g. $\text{Hg}(\text{CH}_3)_2$ and ionic mercury e.g. Hg^{2+} is associated with elevated blood pressure and abnormal heart beats (rhythms).
11. Gastrointestinal system effects: The following range of effects are observed:
- Nausea
 - Vomiting
 - Severe abdominal cramps
 - Diarrhea
 - Corrosive ulceration
 - Bleeding and necrosis of gastro intestinal tract
 - Inflammation and necrosis of the stomach tissue
- All these may cause shock and circulatory collapse
12. Respiratory tract effect: This results via inhalation. A symptom of respiratory tract effects includes:
- Coughing
 - Congestion
 - Bronchitis
 - Pneumonia
 - Chest pain
 - Reduced vital capacity
 - Respiratory failure
 - Death. Etc

Health effects of mercury on children

Children and the fetus are more susceptible to Hg poisoning than adults. Some of the effects include:

- a. Irreversible impairment of the brain
- b. Reduced attention span, language and visual skills

- c. Reduced memory and coordination
- d. High exposure could result in brain damage, mental retardation, blindness, seizures, and speech problems
- e. Weakened heartbeat and immune system.

Environmental effect of mercury

Mercury vapour renders the air hazardous. Ionized forms of mercury are strongly adsorbed by soils and sediments and are desorbed slowly. This implies long residence time in the soil. Clay minerals adsorb Hg maximally at pH 6.0. Iron oxides adsorb mercury in neutral soils. When organic matter content of the soil is very reduced, mercury becomes relatively mobile in acid soils, and evaporation to the atmosphere as well as leaching to ground water are enhanced.

Ionic mercury deposits from the atmosphere are water soluble. Aquatic organisms e.g. fish and mammals easily absorb and accumulate methyl mercury when ingested via food chain.

Safety threshold of mercury

1. The acceptable daily intake is approximately 0.01mg for a 70kg adult.
2. The provisional tolerable weekly intake (PTWI) has been reduced from 3.3 mg per kg body per week to 1.6 mg per kg body per week.

Note: These values are usually reviewed and reduced periodically by international bodies.

COBALT AND THE ENVIRONMENT

Chemistry of cobalt

cobalt has a melting point of 1495°C, boiling point of 2870°C, specific gravity of 8.2 g/cm³ at 20°C, atomic number of 27, atomic weight of 58.933 g/mol and is denoted by the symbol Co. cobalt is hard, ductile and lustrous bluish-grey in color.

Cobalt is an essential element. It is very beneficial to man, being an integral component of vitamin B12. It is therefore required for good health. Deficiencies of Co in man can lead to the following conditions:

1. Anemia
2. Structural alteration of bucal cavity tissue
3. Degeneration of the peripheral nervous system
4. dermal hypersensitivity

Uses of cobalt

1. In the manufacture of many alloys such as super alloys used in gas turbine, aircraft engines, corrosion resistant alloys, high speed steels and cemented carbides.
2. In magnetic recording media
3. As catalysts for the petroleum and chemical industries
4. As drying agents for paints and inks
5. Co is used as pigment in porcelain, pottery, glass, tiles, and enamel jewellery, mostly as cobalt blue
6. Radioactive isotopes, cobalt-60, is used in medical treatment and for food preservation
7. Treatment of anemia

Occurrence of cobalt

Cobalt occurs naturally in the environment, in air, water, rocks, plants and animals. Most of the earth cobalt is in its ore. It is of relatively low abundance in the earth crust and in the natural waters. It is found in nature together with nickel, lead, copper and arsenic. Hence, Co is not found alone and tends to be produced as a by-product of Ni and Cu mining activities.

The main ore of Co are;

- Cobaltite
- Erythrite
- Glauco-dot
- Skutterudite

The world major producers of cobalt are:

- The Democratic Republic of Congo
- China
- Zambia
- Russia
- Australia

Occupational exposure to cobalt

The population, who work in places such as:

- Mining and refining of cobalt
- Production of alloys
- Production of tungsten carbide
- Jewellery producers
- Ceramics, porcelain producers
- Metallurgical industries

Are susceptible to occupational exposure to cobalt.

Non-occupational exposure to cobalt

As cobalt is widely dispersed in the environment, population not working with the metal may be exposed to it by:

- Inhalation (breathing)
- Water consumption
- Food consumption
- Skin contact with contaminated soil or water

Health effect of cobalt to man

Cobalt is beneficial to man as earlier stated. It stimulates the production of red blood cells, thus, used to treat anemia. However, too high concentration of the metal may damage human health.

In soil, it may adsorb on soil particles and is only mobilized under acidic condition (reduced pH). Cobalt is also adsorbed on sediments.

Cobalt may accumulate in plants and in the bodies of animals that eats these plants. Cobalt is not known to bio-magnify up to the food chain, hence, fruits, vegetables, fish and other animals will usually not contain very high amount of cobalt.

Safety threshold for cobalt

1. Relevant agencies such as occupational safety and health administration (OSHA), American conference for governmental and industrial hygienists (ACGIH) and National institute for occupational safety and health (NIOSH) have recommended the range of 0.05 to 0.1 mg/m³ as the safety threshold for cobalt in workplace air for a 8 to 10-hour work day, 40-hr work week.
2. In drinking water and many foods: 0.1 to 5.0 mg/L or mg/kg
3. Recommended dietary intake for infants, children and adults are:
 - 0-12 months = 4 to 5mg
 - 1-10 years = 6 to 10mg
 - 11-18 years = 11-15mg
 - >18 years = 15mg

ZINC AND THE ENVIRONMENT

CHEMISTRY OF ZINC

Zinc is a lustrous bluish-white metal whose atomic number and atomic mass are 30 and 65.37 g/mol respectively. The density is 7-11 g/cm³ at 20°C with melting and boiling points at 420°C and 907°C respectively. The predominant valence is +2. Zinc is brittle and crystalline at ordinary temperature but becomes ductile and malleable between 110°C and 150°C. It is denoted by the symbol Zn.

Uses of zinc

- It is used principally for galvanizing, about 50% of metallic zinc goes into galvanizing steel
- Zn is also important in the preparation of alloys
- It is used for the negative plates in some electric batteries
- Zinc is utilized for roofing and gutters in building construction
- Zinc oxides are used as a white pigment in paints
- Zinc is used as a pigment in plastic, cosmetics, photocopier paper, wallpaper, printing inks
- It is utilized as a catalyst during rubber production and as a heat disperser in the final product
- Zinc is used as drugs, as it is believed to possess anti-oxidant properties which protect against premature aging of the skin and muscle of the body.

Occurrence of zinc

Zinc is the 23rd most abundant element in the earth's crust. It occurs naturally in air, water and soil but the mineral ores give more of the metal. The dominant ore is zinc blende, known as sphalerite. The other ores are wurtzite, smithsonite and hemimorphite. Zinc is largely mined in:

- Canada
- Russia
- Australia
- USA
- Peru

Occupational exposure to zinc

This occurs principally from industrial sources or workplace. Hence all workers that have to do with zinc as earlier stated are exposed to it occupationally. Examples are miners, coal and waste combustion workers etc.

Non-occupational exposure

This occurs essentially through many foodstuffs and contaminated drinks which may be higher when it is stored in metal tanks.

Health effects of zinc

The absorption of too little Zn can cause these:

- Loss of appetite
- Decreased sense of taste and smell
- Slow wound healing
- Skin sores
- Birth defect

Zinc is an essential trace element required for the function of over 200 metallo-enzymes. Zinc is also important in the regulation of DNA and RNA synthesis via interaction with DNA binding protein. It also plays a critical role in hormone-receptor interaction

Some zinc salts are used in the treatment of:

- Leg ulcer
- Wilson disease
- Prevention on non-steroidal anti-inflammatory drug-induced gastrointestinal damage.

Despite these, too much zinc can cause eminent health problems. The important zinc salts toxicology are:

- Zinc chloride ($ZnCl_2$)
- Zinc oxide (ZnO)
- Zinc sulphate ($ZnSO_4$)

The health related problems of zinc salts are;

- Stomach cramps
- Skin irritation
- Vomiting
- Nausea
- Anemia
- Respiratory disease
- Eye irritation
- Fatigue

Very high level of zinc can cause:

- Damage the pancreas
- Disturb the protein metabolism
- Cause arteriosclerosis.

In the workplace, inhalation of Zn dust can lead to a flu-like condition known metal fever. Zinc can be a danger to unborn and newborn babies.

Environmental effect of zinc

Zinc in water (from wastewater of industrial plants) increases the acidity of waters. Some fish can accumulate Zn in their bodies, when found in zinc contaminated waterways. Zinc in fish can bio-magnify and enter in food chain.

Insoluble zinc in soils can contaminate groundwater. Large concentrations of zinc in soils of farmland pose health threat to animals and plants also (apart from groundwater contamination).

Like Cu, Zn interrupts the activity in soils by its negative influence on the activities of microorganism and earthworms. It also slows down the breakdown of organic matter in soil.

Safety threshold

Recommended daily intakes

1. Infants and children: 2 to 8mg
2. Adults: 9 to 13mg, it could be as high as 40mg
3. water: It could be as high as 1.0mg/L

