HEAVY METALS AND ITS EFFECTS ON VEGETATION AND ENVIRONMENT

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INTRODUCTION

- Heavy metals are natural constituents of the earth's crust , but indiscriminate human activities have drastically altered their geochemical cycles and biochemicals balance.
- Any toxic metals may be called heavy metals.
- Since heavy metals have a propensity to accumulate in selective body organs.
- The average safety levels in food or water are often misleading high.

DEFINITION

- Heavy is any metal or metalloid of environmental concern.
- Heavy metals are metallic element that have relatively high density usually greater than 5 g/cm^3, or their density is greater than the density of water.
- The term originated with reference to the harmful effects of arsenic, beryllium, cadmium, chromium, lead, mercury, nickel and selenium are some of the metals persists in nature and causes damage or death in animals, humans and plants even at very low concentrations.

Heavy metals

Macro-nutrient elements	• cobalt (Co), copper (Cu) • zinc (Zn) and iron (Fe).
Micronutrient elements	• copper (Cu), nickel (Ni), • chromium (Cr) and iron (Fe)
Highly toxic elements	• cadmium (Cd), lead (Pb), • silver (Ag) and mercury (Hg)
Precious elements	• platinum, silver and gold

PROPERTIES OF HEAVY METALS

- They occur near the bottom of the periodic table.
- Have high densities.
- Toxic in nature.
- Nondegradable.

Note : Arsenic is not actually a metal but is a semimetal i.e., its properties are intermediate between those of metals and nonmetals.

Heavy Metal Pollution

- Environmental pollution by metals with a high atomic mass, such as lead and mercury is known as ***heavy metal pollution***
- These metals come from a number of sources, including lead in petrol, industrial effluents, and leaching of metal ions from the soil into lakes and rivers by acid rain.
- 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.

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.

What causes heavy metal pollution?


Mining waste


Industrial waste


Sediment from solid waste

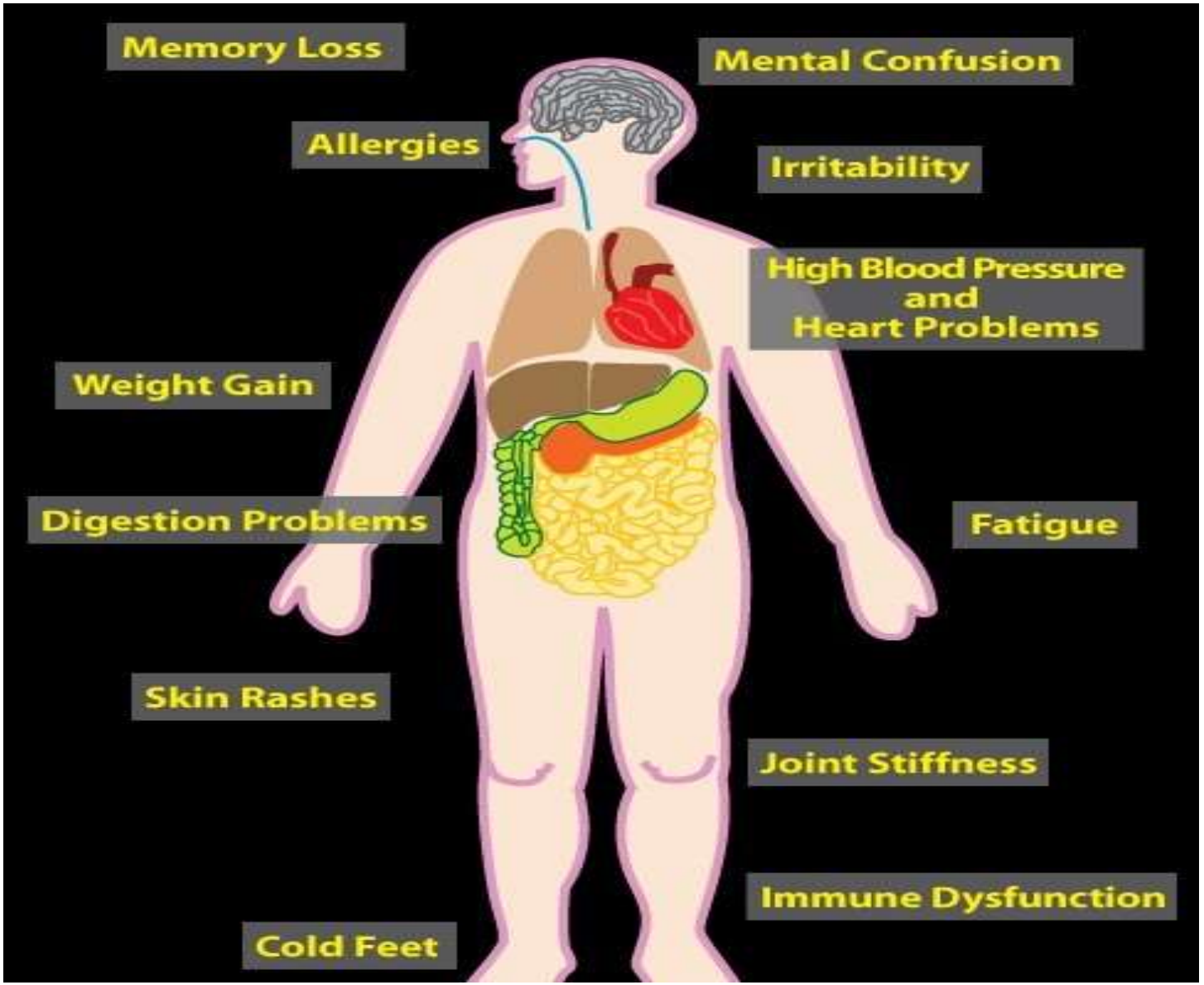
HEAVY METALS AND LIVING ORGANISMS

- Living organisms require varying amounts of heavy metals. Iron, copper, manganese and zinc are required by humans.
- All metals are toxic at higher concentrations and can cause damaging to the organisms.
- For example plutonium, and lead are toxic metals that have no known vital or beneficial effects and organisms.
- They accumulate and thus disturb function in vital organs and glands of our body such as heart, brain, kidneys, bone, liver, etc.
- They dislocate vital nutritional minerals from their original place and thus hinder their biological function.
- There are many ways by which these toxins can be introduced into the body such as by consumption of different food products, exposure to household products, personal products and varying numbers of industrial products and chemicals.

Sources of heavy metal pollutants

Effects of heavy metals on Humans

- 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)
  - respiratory system issues (respiratory tract cancers)
  - reproductive problems
  - immune system deficiencies
  - decreased white blood cell count.
- Other problems associated with metal pollution are:
  - hair loss (alopecia),
  - skin disorder (rashes, irritated skin),
  - poor memory,
  - difficulty in understanding abstract ideas or carrying out complex commands),
  - nervous system,
  - physiological impairment (nerve conductivity etc),
  - motor disorders (difficulty in walking, talking and swallowing,
  - jerks,
  - loss of balance, problems with sitting or lying etc),
  - sensory abnormalities,
  - hearing loss,
  - blurred vision and sensitivity to light.


Memory Loss
Mental Confusion
Allergies
Irritability
High Blood Pressure and Heart Problems
Weight Gain
Digestion Problems
Fatigue
Skin Rashes
Joint Stiffness
Immune Dysfunction
Cold Feet

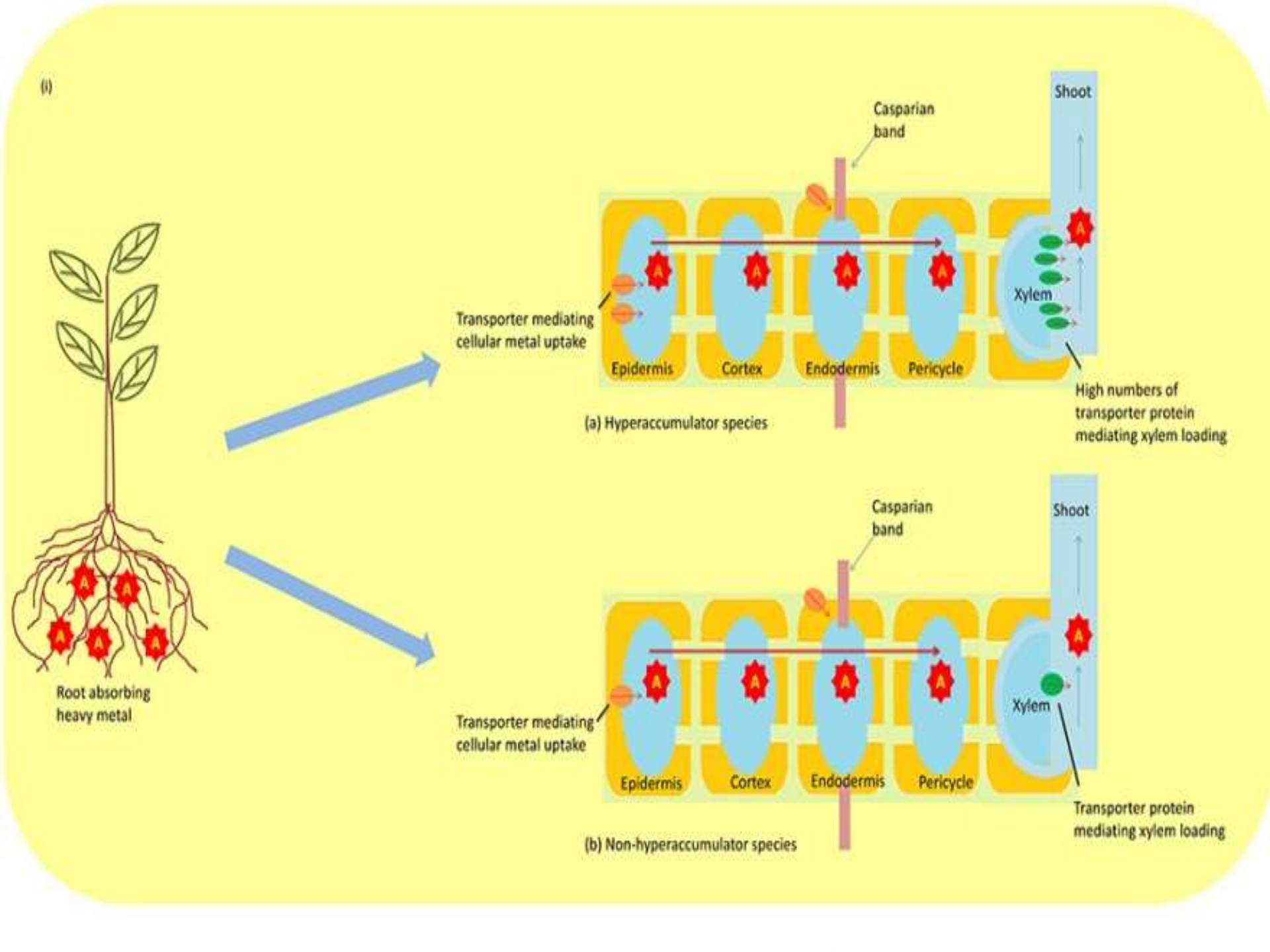
TYPES OF HEAVY METALS AND THEIR PERMISSIBLE LIMITS

Pollutants	*Major sources*	*Effect on human health*	*Permissible level (mg/l)*
Arsenic	Pesticides, fungicides, metal smelters	Bronchitis, dermatitis, poisoning	0.02
Cadmium	Welding, electroplating, pesticide fertilizer, Cd and Ni batteries, nuclear fission plant	Renal dysfunction, Lung disease, Lung cancer, Bone defects (Osteomalacia, Osteoporosis), increased blood pressure , kidney damage, bronchitis, gastrointestinal disorder, bone marrow, cancer	0.06
Lead	Paint, pesticide, smoking, automobile emission, mining, burning of coal	Mental retardation in children, developmental delay, fatal infant encephalopathy, congenital paralysis, sensor neural deafness and, acute or chronic damage to the nervous system, epilepticus, liver, kidney, gastrointestinal damage	0.1
Manganese	Welding, fuel addition, ferromanganese production	Inhalation or contact causes damage to central nervous system	0.26
Mercury	Pesticides, batteries, paper industry	Tremors, gingivitis, minor psychological changes, acrodynia characterized by pink hands and feet, spontaneous abortion, damage to nervous system, protoplasm Poisoning	0.01
Zinc	Refineries, brass manufacture, metal Plating, plumbing	Zinc fumes have corrosive effect on skin, cause damage to nervous membrane	15
Chromium	Mines, mineral sources	Damage to the nervous system, fatigue, irritability	0.05
Copper	Mining, pesticide production, chemical industry, metal piping	Anemia, liver and kidney damage, stomach and intestinal irritation	0.1

Metals uptake in plants

- Metal ions cannot move freely across the cellular membranes, which are lipophilic structures because of their charge.
- Therefore, ion transport into cells must be mediated by membrane proteins with transport functions, generically known as transporters.
- These transporters possess an extracellular binding domain to which the ions attach just before the transport, and a trans-membrane structure which connects extracellular and intracellular media.
- The binding domain is receptive only to specific ions and is responsible for transporter specificity.

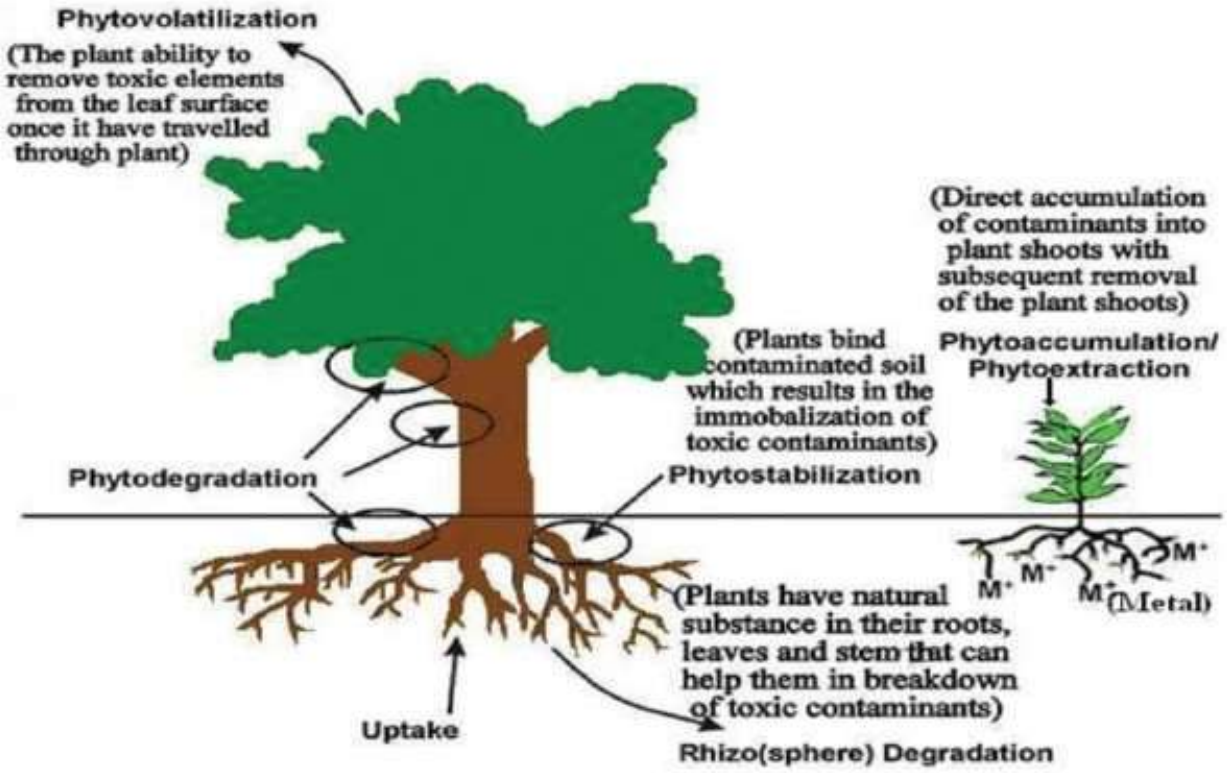
- The trans-membrane structure facilitates the transfer of bound ions from extracellular space through the hydrophobic environment of the membrane into the cell.
- It is important to note that of the total amount of ions associated with the root; only a part is absorbed into cells.
- A significant ion fraction is physically adsorbed at the extracellular negatively charged sites (COO^-) of the root cell walls.
- The cell wall-bound fraction cannot be translocated to the shoots.


(i)
Root absorbing heavy metal
Transporter mediating cellular metal uptake
Casparian band
Shoot
Xylem
Epidermis
Cortex
Endodermis
Pericycle
High numbers of transporter protein mediating xylem loading
(a) Hyperaccumulator species
Transporter mediating cellular metal uptake
Casparian band
Shoot
Xylem
Epidermis
Cortex
Endodermis
Pericycle
Transporter protein mediating xylem loading
(b) Non-hyperaccumulator species

HEAVY METALS EFFECTS ON PLANTS

- Plant experiences oxidative stress upon exposure to heavy metals that leads to cellular damage and disturbance of cellular ionic homeostasis .
- To minimize the detrimental effects of heavy metals exposure and their accumulation, plants have evolved detoxification effect mainly based on chelation sub-cellular compartmentalisation

MECHANISM OF HEAVY METAL ACCUMULATION BY PLANTS



LIMITS OF HEAVY METALS IN PLANT SPECIES

NAME OF THE HERBS	BOTANICAL NAME	PERMISSIBLE LIMITS(PPM)
Arjuna	Terminalia arjuna	20
Arachis oil	Arachis hypogaea	10
Ashwagandha	Withania somnifera	20
Gokhru	Tribulus terrestris	20
Tulsi	Ocimum sanctum	20

HEAVY METALS CONTAMINATION OF VEGETABLES

 Heavy metals contamination of vegetables cannot be underestimated as these foodstufs are important of human diet.

 Vegetables are rich sources of vitamins, minerals and fibers, and also have beneficial antioxidative effects.

 Heavy metals contamination of food is one of the most important aspects of food quality assurance.

General Effects

- Plant growth is commonly used as a general parameter to study the influence of stressors, with growth rate inhibition often being the most obvious plant reaction.
- This is especially true of the root system, which is the first plant system to come into direct contact with toxic ions.

Fodor Model

- **Fodor** (2002) suggested an interesting stepwise model for the action of heavy metals in plants. This model has the advantage that visible effects are linked to metabolic events that are influenced by the metal ion of interest.
- Following are the stages given by Fodder;
  1. At this stage metal ions enter in to the plants and cause the formation of reactive oxygen species (ROS) and effect the membranes.
  2. the metal ion reacts with all possible interaction partners within the cytoplasm, including proteins, other macromolecules.
  3. At stage 3 is mainly related to the factors that influence homeostatic events, including water uptake, transport and transpiration. At this stage, symptoms start to develop
  4. Now symptoms become visible.
  5. At stage 5, the death of the plant occur.

Effect on activity of enzymes

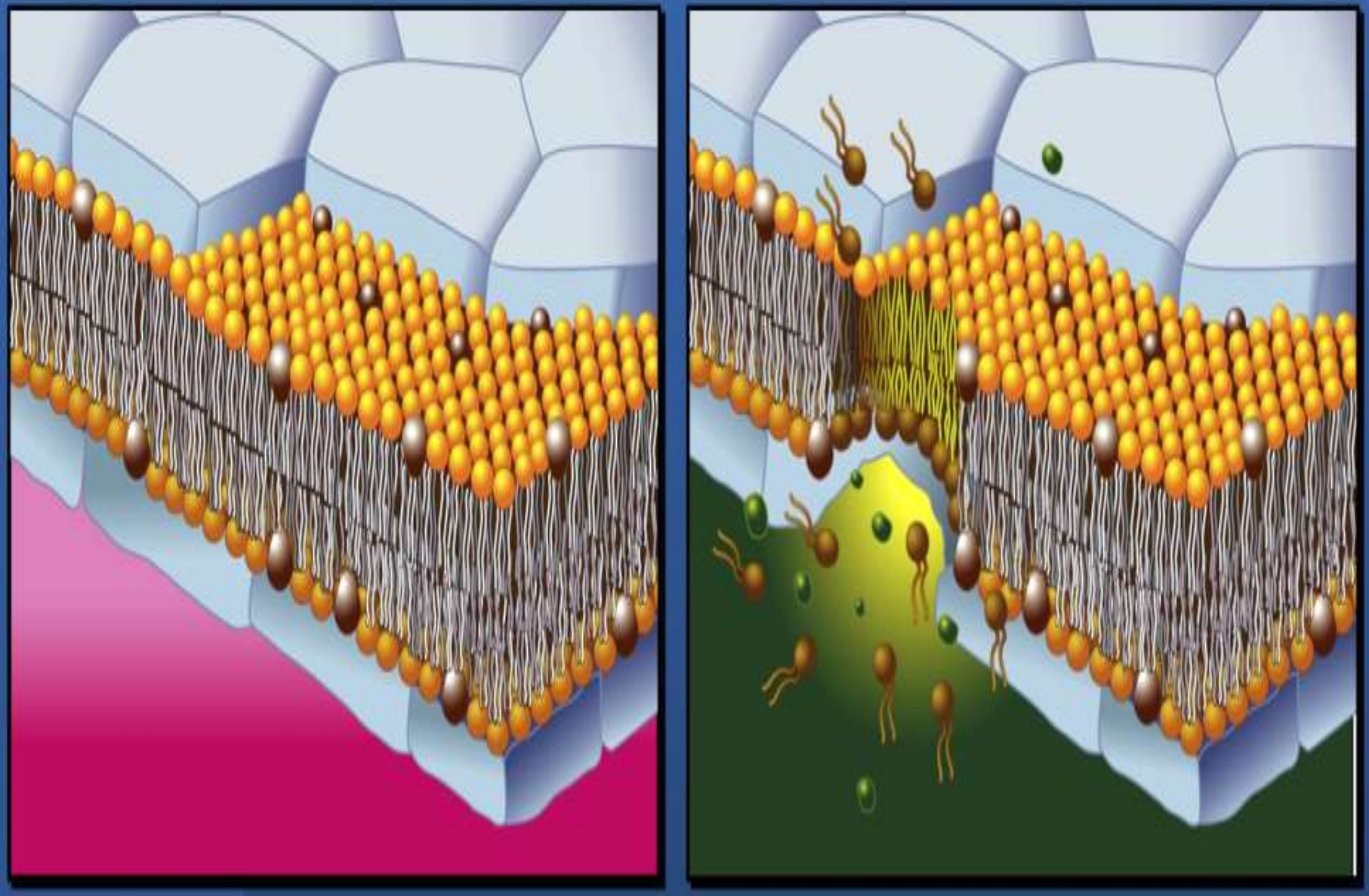
- Another important mechanism of heavy metal toxicity is the ability of heavy metals to bind strongly to oxygen, nitrogen, and sulfur atoms. Because of these features, heavy metals can inactivate enzymes.
- For example, Cd binding to sulfhydryl groups of structural proteins and enzymes leads to misfolding and inhibition of their activity.
- The displacement of one heavy metal ion by another leads to the inhibition or loss of enzyme activities.
- Divalent cations such as Co^{+2}, Ni^{+2}, and Zn^{+2} displace Mg^{+2} in ribulose 1,5- bisphosphate carboxylase/oxygenase (Rubisco) and result in a loss of activity.

Membrane damage

- Additionally, heavy metals cause membrane damage through various mechanisms, including the oxidation of and cross-linking with protein and cause changes in the composition of membrane.

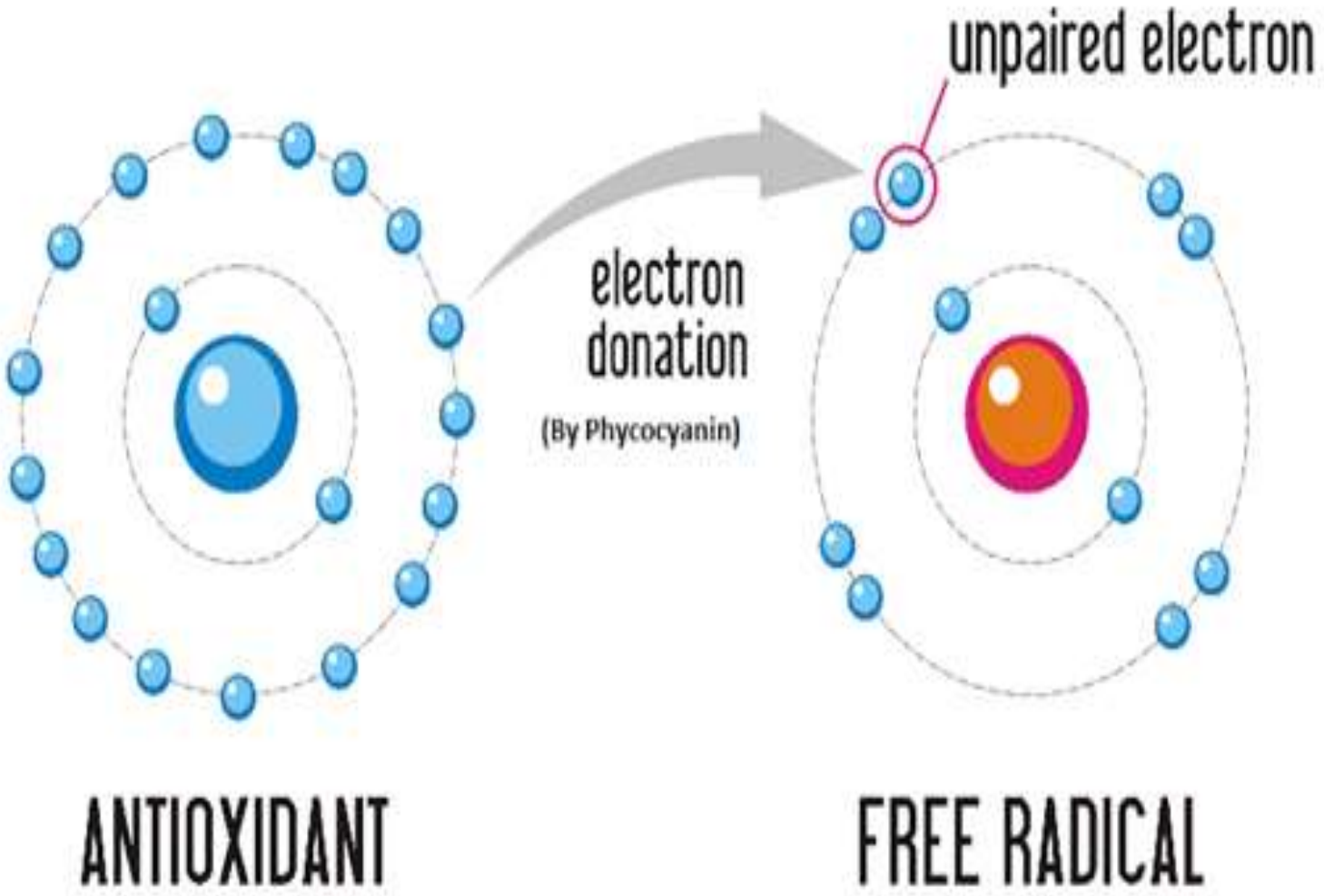
Healthy Membrane

Oxidative Stress Damage

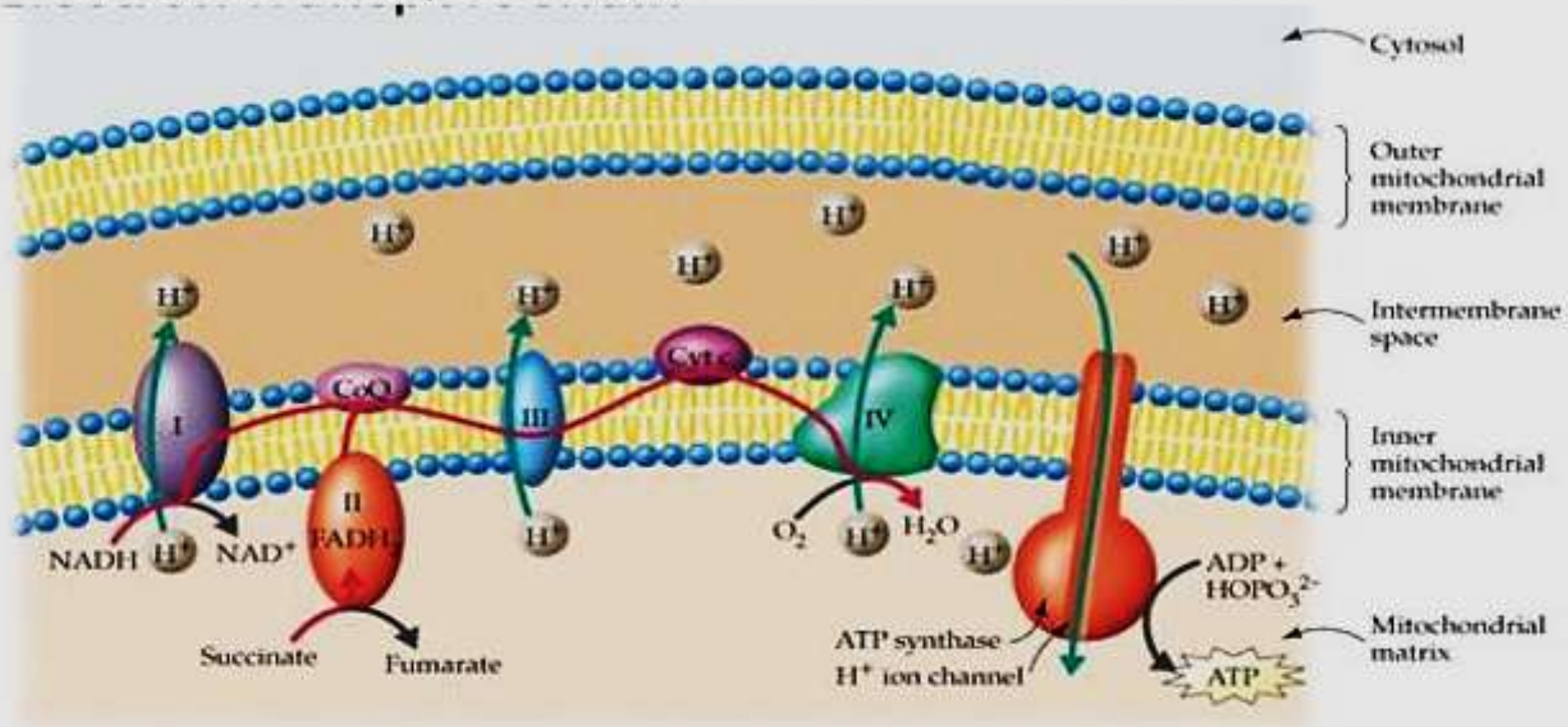


Formation of Reactive Oxygen Species

- Heavy metals caused the formation of reactive oxygen species. The main important ROS (O^{-2}) and the hydroxyl radical (OH^{-}), because both are highly reactive, carrying out oxidation reactions with many organic molecules.
- The generation of ROS is a general phenomenon; higher plants developed a highly sophisticated antioxidant system during the course of evolution.
- This consists of several enzymes (catalase, oxidase, peroxidases and reductase) and antioxidant substrates (ascorbate and a-tocopherol).
- The main sources of ROS under control conditions (an absence of toxic concentrations of heavy metals) are photosynthetic and respiratory electron transport processes.


unpaired electron
electron donation
(By Phycocyanin)
ANTIOXIDANT
FREE RADICAL

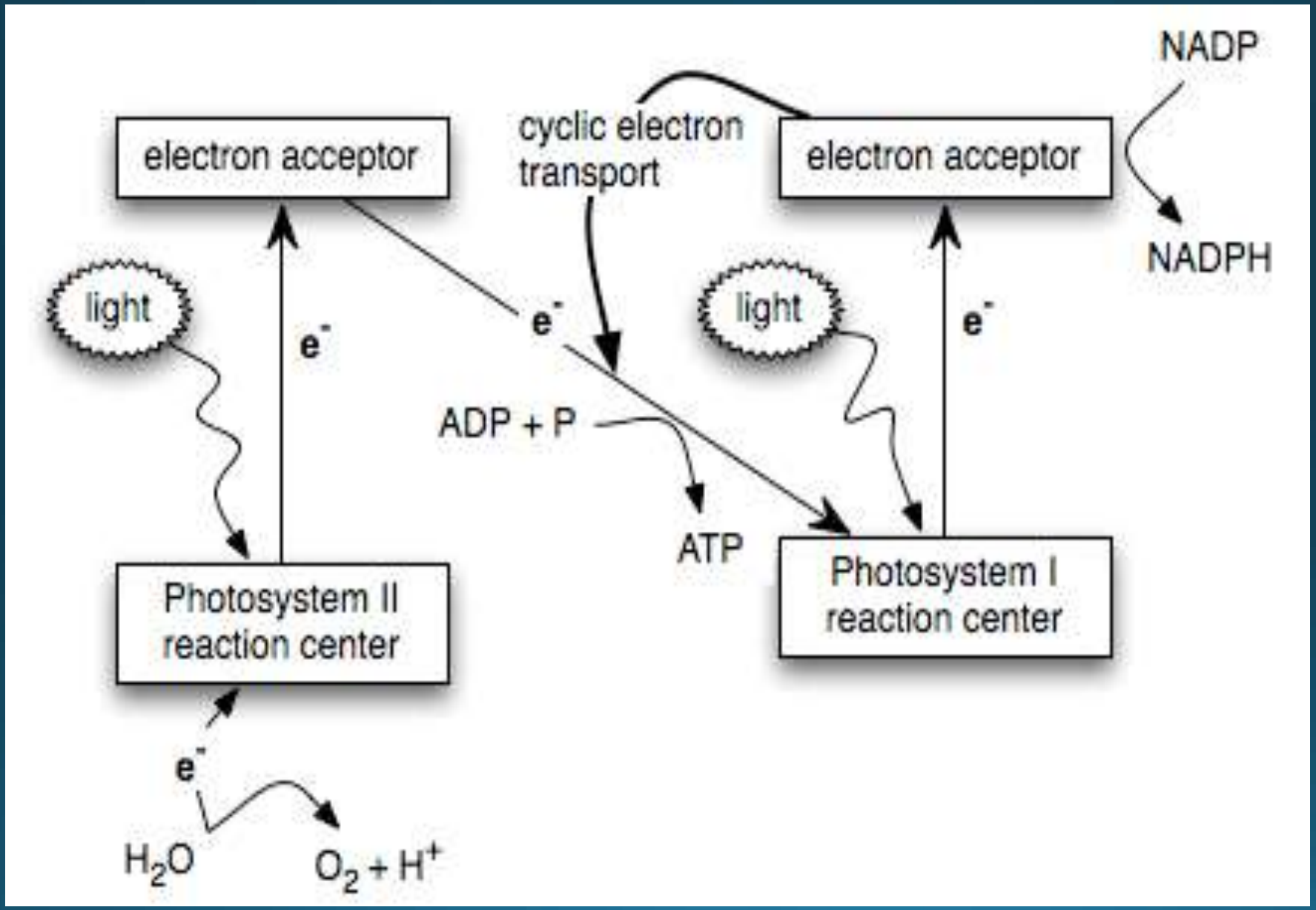
Superoxide Production from Mitochondrial Electron Transport Chain



Leaking' of electron (to oxygen) during electron transport leads to the formation of $O_2^{\bullet-}$ ($O_2 + e^- \longrightarrow O_2^{\bullet-}$)

Photosynthesis

- Inhibition of photosynthesis is one effect that most of the heavy metals have in common when present at toxic concentrations.
- It is a very sensitive response. Measuring the photosynthetic activity is a good screening method for detecting possible stress situations, perhaps including those involving heavy metals.
- Direct effects of heavy metals on light and dark reactions and indirect effects caused by them decreasing the photosynthetic pigment content are involved.
- Several enzymes involved in the Calvin cycle are also inhibited, especially Rubisco and PEP carboxylase.


NADP
electron acceptor
cyclic electron transport
electron acceptor
NADPH
light
e⁻
e⁻
light
e⁻
ADP + P
ATP
Photosystem II reaction center
Photosystem I reaction center
e⁻
H2O
O2 + H+

HEAVY METALS AND ENVIRONMENTAL POLLUTION

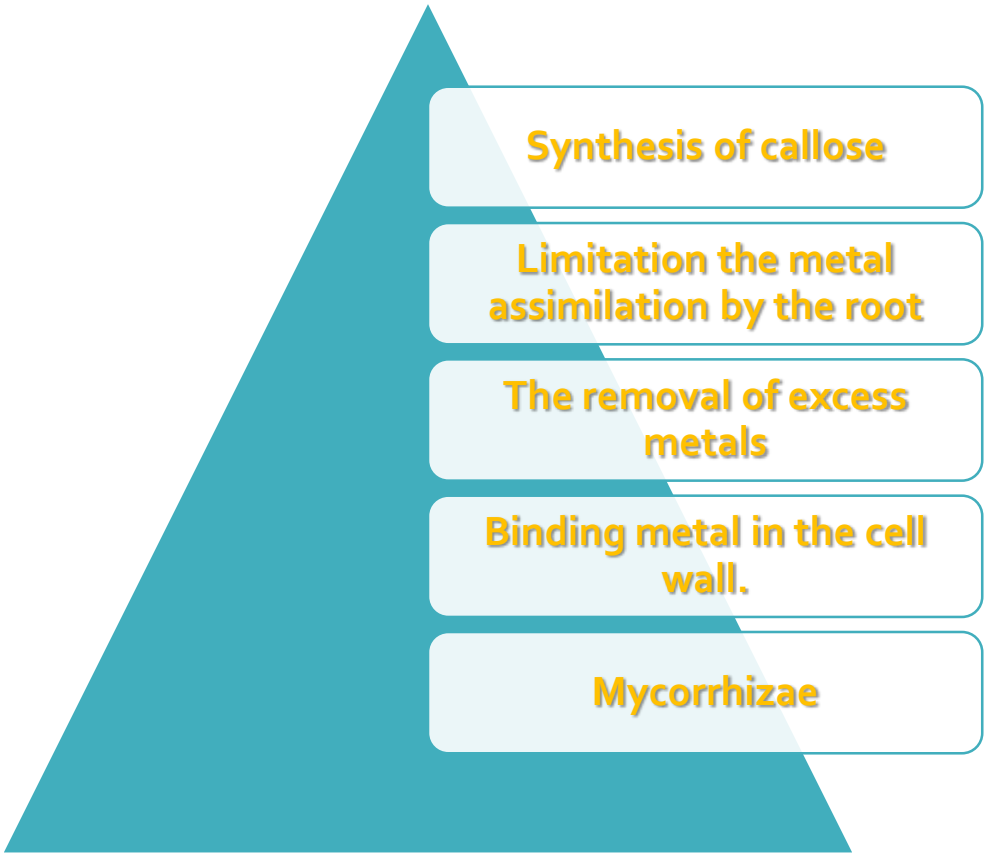
- Metal concentration in soil typically ranges from less than one to as high as 100,000mg/kg.

- Heavy metals are the main group of inorganic contaminants large area land contaminated with them due to use of pesticides, fertilizers and emission from municipal waste incinerates and smelting industries.

HEAVY METALS EFFECTS ON WATER AND CONSEQUENCES

- Heavy metals occurs in the geological structures, and can therefore enters water resources through natural processes.
- For example, heavy rains or flowing water can leach heavy metals out of geological formations.
- This processes are exacerbated when this geology is distributed by economic activities such as mining.
- These can be mined - out area to water and air, and can lead to consequences such as acid mine drainage (AMD).

Defense mechanism in plants against metal toxicity



Synthesis of callose

- In the plant cell, the earliest defence reaction in the case of heavy metal presence is a synthesis of callose (β-1,3 glucan).
- This polysaccharide is deposited on the outside of the cell membrane, thereby reducing the diffusion of metal ions into the cell.
- The enzyme, which is involved in the synthesis of callose, is β-1, 3-glucan synthetase.

Limitation of metal assimilation by the roots

- Another defense mechanism is to limit the metal assimilation from the environment by the roots.
- In an environment contaminated with heavy metals plant roots secrete a number of substances that can bind ions and limit their assimilation by plants.
- Among such compounds are organic acids, and substances present in root extracellular matrix composed mainly of e.g. simple sugars, phenols, amino acids and polysaccharide gels.
- Another way to reduce the toxicity of metals is the ability of roots to change the rhizosphere PH. The increased pH causes a decrease in the availability of metals.

The removal of excess metals

- Another strategy is the ability of plants to remove excess metals in the form of crystals by salt glands of the leaf epidermis.
- For example, copper, nickel, zinc, iron and manganese can be removed in such a way.
- Metals may also be transported to the ageing leaves and removed along with them.

Binding metal in the cell wall

- Another plant defence mechanism against the toxic effects of heavy metals is its binding in the cell wall. For some species, 80–95% of the metal taken up by the cells can be fixed (this particularly applies to ions of lead, copper and zinc).
- The cell walls are composed of pectins, which contain many of the methylated ($COOCH_3$) carboxyl groups, hemicelluloses and cellulose.
- Their dissociation leads to the appearance of negatively charged groups, which are typically saturated with calcium.
- In the presence of heavy metals (Cd^{+2}, Pb^{+2}, Cu^{+2}) calcium ions may be competitively replaced by metals cations. In this way, toxic metal ions are immobilized in the cell wall

Mycorrhizae

- Another mechanism, known as mycorrhizae, enables symbiotic relationships between non-pathogenic fungi and roots of higher plant.
- Research studies have shown that mycorrhizae fungi are able to alleviate the stress of heavy metals.

Individual effects of Heavy Metals

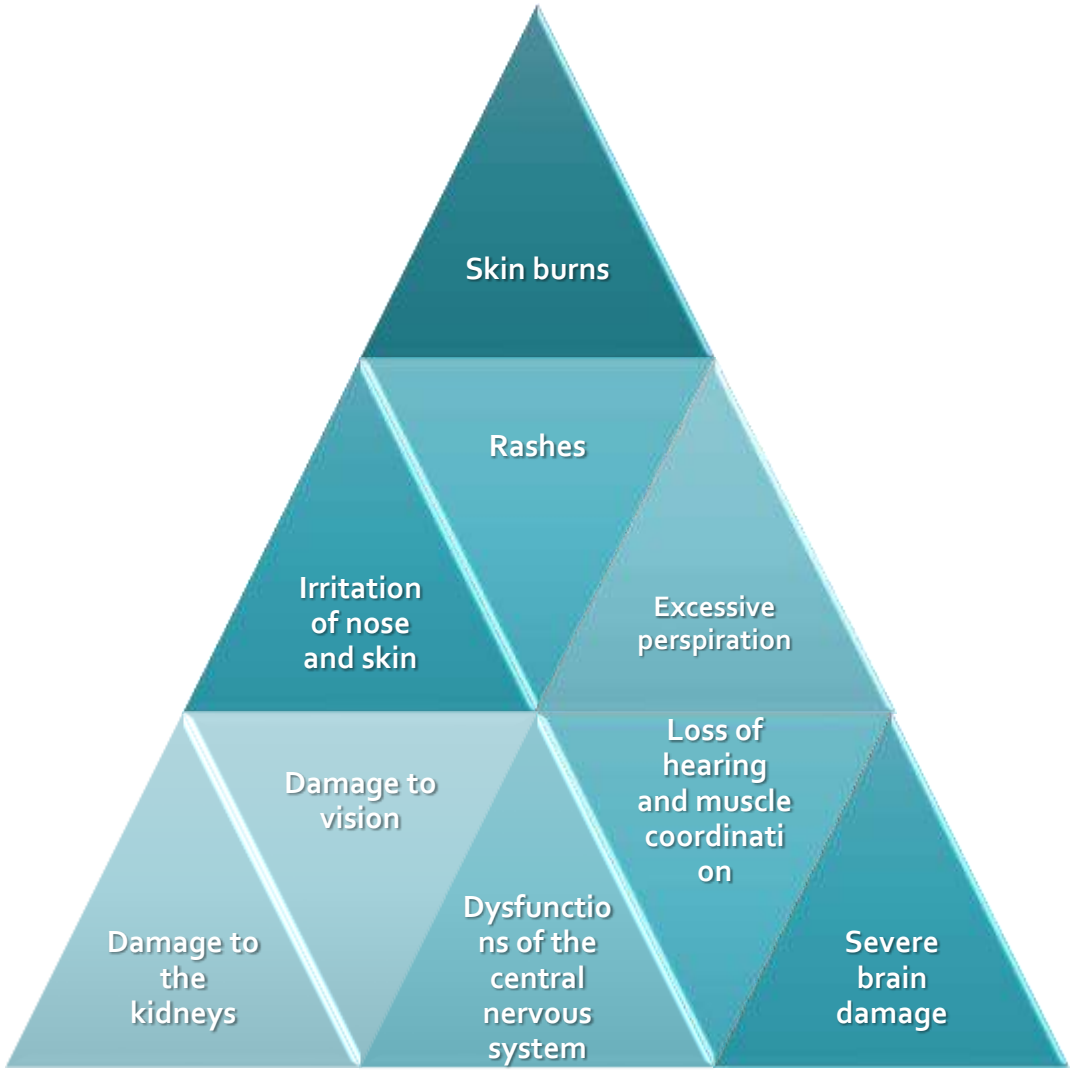
Mercury

- Most volatile of all metals
- Highly toxic in vapor form
- Liquid mercury itself is not highly toxic, and most of that ingested is excreted

Sources of Mercury

- Elemental mercury is employed in many applications due to its unusual property of being a liquid that conducts electricity
- Used in electrical switches, fluorescent light bulbs and mercury lamps
- Emission of mercury vapor from large industrial operations
- Unregulated burning of coal and fuel oil
- Incineration of municipal wastes
- Emissions from mercury containing products :batteries, thermometers, etc.
- Mercury amalgams: dental fillings

Health effects



Environmental effects of mercury

- Acidic surface waters can contain significant amounts of mercury
- When the pH values are between five and seven, the mercury concentrations in the water will increase due to mobilisation of mercury in the ground
- Once mercury has reached surface waters or soils microorganisms can convert it to methyl mercury, a substance that can be absorbed quickly by most organisms and is known to cause nerve damage

Environmental effects of mercury

- Fish are organisms that absorb great amounts of methyl mercury from surface waters every day (mercury can accumulate in fish and in the food chains)
- **The effects that mercury has on animals are:** kidneys damage, stomach disruption, damage to intestines, reproductive failure and DNA alteration

Lead

- Has a very low melting point of 327 degrees Celsius
- Used as a structural metal in ancient times and for weather proofing buildings
- Romans used it in water ducts and in cooking vessels
- Analysis of ice-core samples from Greenland indicate that atmospheric lead concentration reached a peak in roman times that was not equaled again until the renaissance

Sources of lead

- Commonly used in the building industry for roofing and flashing and for soundproofing
- Used in pipes
- When combined with tin, it forms solder, used in electronics and in other applications to make connections between solid metals
- Lead is also used in ammunition

  Note: Lead shots have been banned in United States, Canada, Netherlands, Norway and Denmark
- Lead is used in batteries and sinkers in fishing

Sources (contd.)

- Used in paints

  Lead chromate is the yellow pigment used in paints usually applied to school buses. Lead is also used in corrosion-resistant paints and has a bright red color

- Used in ceramics and dishware

  The leaching of lead from glazed ceramics used to prepare food is a major source of dietary lead, especially in Mexico

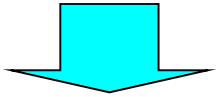
- In the past, lead salts were used as coloring agents in various foods
- Lead is used in some types of PVC mini-blinds

Health effects

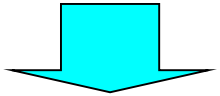
- At high levels, inorganic lead is a general metabolic poison
- Lead poisoning effects the neurological and reproductive systems, example: downfall of roman empire
- Lead breaks the blood-brain barrier and interferes with the normal development of brain in infants
- Lead is observed to lower IQ levels in children
- Lead is transferred postnatally from the mother in her breast milk
- At elevated levels, lead poisoning would eventually result in death

Environmental effects of lead

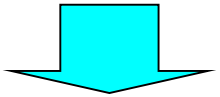
Lead accumulates in the bodies of water organisms and soil organisms



Health effects on shellfish can take place even when only very small concentrations of lead are present



Body functions of phytoplankton can be disturbed when lead interferes. Phytoplankton is an important source of oxygen production in seas and many larger sea-animals eat it



That is why we now begin to wonder whether lead pollution can influence global balances

Heavy metals analyzed

Cadmium (Cd), Chromium (Cr), Copper (Cu), Mercury (Hg), Manganese (Mn), Nickel (Ni), Phosphorus (P), Lead (Pb), Zinc (Zn).

(Metals Found in Higher Concentrations in Urban Soils).

Soil Profile

(0-201cm).

- Surface Horizons: "O" &"A"
- Subsoil Horizon: "B"
- Substratum Horizons: "C" "D" (threshold).

Cadmium

- Cadmium lies in the same subgroup of the periodic table as zinc and mercury, but is more similar to zinc
- Coal burning is the main source of environmental cadmium
- Incineration of wastes containing cadmium is an important source of the metal in the environment
- Cadmium is most toxic in its ionic form unlike mercury

  Note: Mercury is most toxic in vapor form and lead, cadmium and arsenic are most toxic in their ionic forms.

Sources of Cadmium

- Cadmium is used as an electrode in "nicad" batteries
- Cadmium is used as a pigment in paints(yellow color)
- It is also used in photovoltaic devices and in TV screens
- Cigarette smoke
- Fertilizers and pesticides

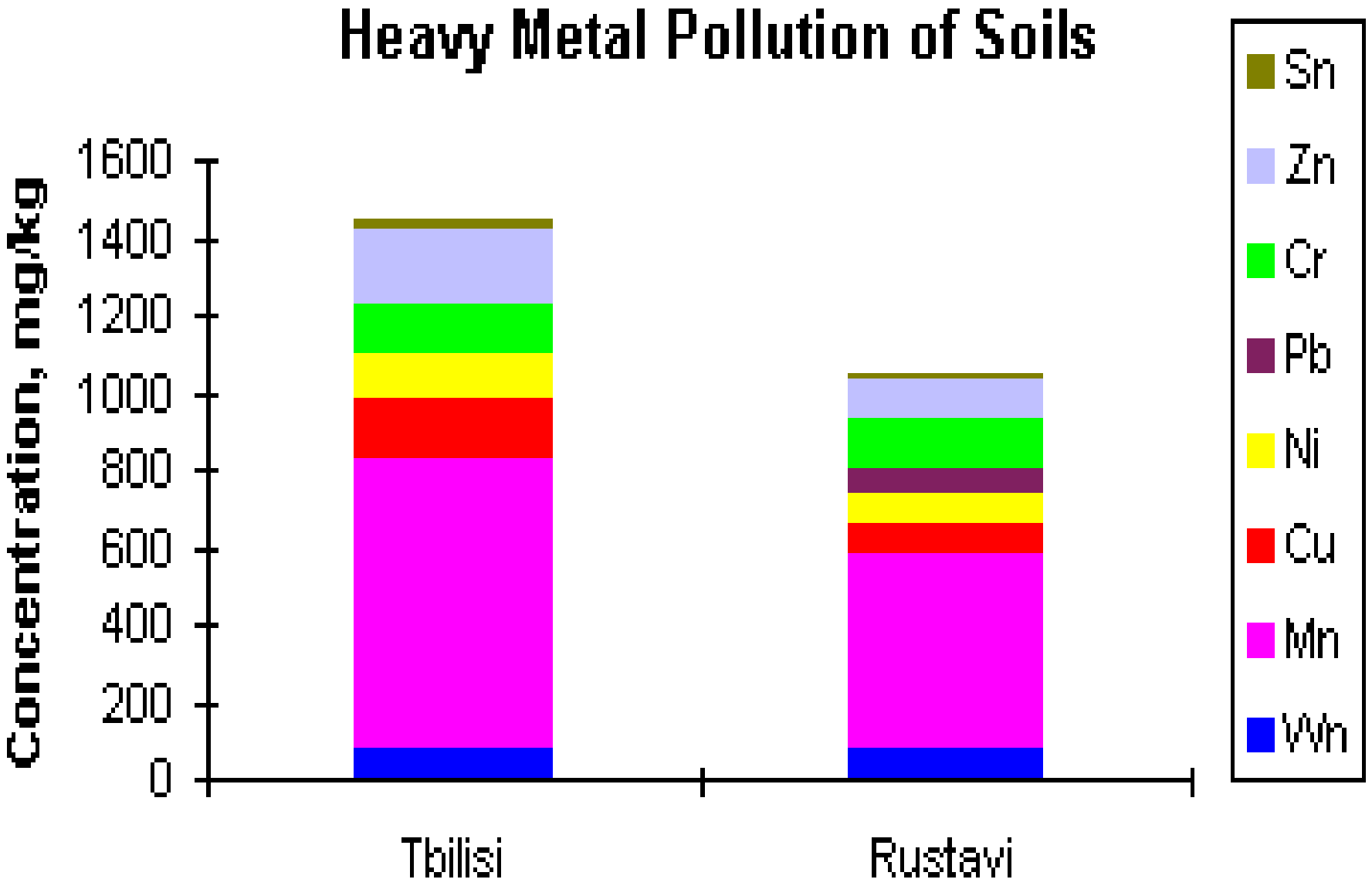
Note: The greatest proportion of our exposure to cadmium comes from our food supply- seafood, organ meats, particularly kidneys, and also from potatoes, rice, and other grains.

Health effects

- Severe pain in joints
- Bone diseases
- Kidney problems
- Its lifetime in the body is several years
- Areas of greatest risk are Japan and central Europe
- In very high levels it poses serious health problems related to bones, liver and kidneys and can eventually cause death.

Environmental effects of cadmium

- Cadmium can be transported over great distances when it is absorbed by sludge
- This cadmium-rich sludge can pollute surface waters as well as soils
- Cadmium strongly adsorbs to organic matter in soils
- When cadmium is present in soils it can be extremely dangerous, as the uptake through food will increase
- Soils that are acidified enhance the cadmium uptake by plants
- This is a potential danger to the animals that are dependent upon the plants for survival – Cadmium can accumulate in their bodies, especially when they eat multiple plants
- In aquatic ecosystems cadmium can bioaccumulate in mussels, oysters, shrimps, lobsters and fish
- The susceptibility to cadmium can vary greatly between aquatic organisms
- Salt-water organisms are known to be more resistant to cadmium poisoning than freshwater organisms


Heavy Metal Pollution of Soils
Concentration, mg/kg
1600
1400
1200
1000
800
600
400
200
0
Tbilisi
Rustavi
Sn
Zn
Cr
Pb
Ni
Cu
Mn
Wn

Arsenic

- Arsenic oxides were the common poisons used for murder and suicide from roman times through to the middle ages
- Arsenic compounds were used widely as pesticides before the organic chemicals era
- Arsenic is very much similar to phosphorous

Sources of Arsenic

- Pesticides
- Mining, smelting of gold, lead, copper and nickel
- Production of iron and steel
- Combustion of coal
- Leachate from abandoned gold mines
- Used as a wood preservative
- Herbicides
- Tobacco smoke
- Wallpaper paste and pigments in wallpaper

Health effects

- Birth defects
- Carcinogen:

  Lung cancer results from the inhalation of arsenic and probably also from its ingestion. Skin and liver cancer, and perhaps cancers of the bladder and kidneys, arise from ingested arsenic
- Gastrointestinal damage
- Severe vomiting
- Diarrhea
- Death

REVIEW OF HEAVY METALS

HEAVY METALS	DESCRIPTION	SOURCE	HEALTH EFFECTS
MERCURY	Most volatile, highly toxic in vapour.	Incineraton of municipal waste, electrical switches, fluorescent light bulbs and mercury bulbs.	Skin burns, damage to the kidneys,severe brain damage, damage to vision.
CADMIUM	It most toxic, it lies in the same sub group of the periodic table.	Cigarette smoke, fertilizer and pesticides, photovoltaic device in tv screens.	Kidney problems, bone diseases, severe pain in joints.
LEAD	Low melting point, structural metal, water ducts in cooking vessels.	Batteries and sinkers in fishing, pipes paints, ceramics.	Neurological and reproductive system effects, blood brain barrier effects.
ARSENIC	Similar to phosphorous, common poison used for murder and suicide.	Pesticides, herbicides, tobacco smoke, wood preservative.	Diarrhea, severe vomiting, GI-damage.

METHODS FOR MEASUREMENT OF TRACE METALS

- Most common method of collecting particulate matter is through filters.
- Identification and concentration of individual trace metals like lead, cadmium, arsenic, mercury and chromium is determined by

  ➡ Atomic absorption spectrophotometry, is a destructive method and requires atleast 1 to2ml of solution.

  ➡ X-ray flourescence, is a nondestructive method and works independent of the chemical state of the sample.

CONTROL METHODS

- Periodic vaccuming of the house can be effective in removal of these pollutants.
- Replacement of wood-burning by an equivalent gas or electrical appliance.
- Removal of old lead and mercury-based paints.
- The effective method for removal of mercury vapours is by the use of packed bed of absorbents.
- Gold-coated denuder can also be used for the removal of mercury from air.

HEAVY METALS CAN BE REMOVED IN THE FOLLOWING MANNER:

Metal	Removing agent	Major method	Other methods
Heavy metals in Water	Natural zeolites, Conductive electroactive Polymers [polypyrrole and polyaniline], Calcium alginate microparticles, Dithiocarbamates, chitosan-capped gold nanoparticles	Ion exchange	Biosorption, immobilization in matrix, complexation, Bioremediation
Chromium ions [mainly from industrial waste]	Activated carbon	Ion-exchange adsorbents	Chemical sedimentation, surface absorption, ion-exchanger and reverse osmosis
Mercury	Activated carbon, Bentonite	Ion exchangers	Reduction, precipitation, extraction and ion exchange
Arsenic	Polypyrrole and its composites, poly(vinyl alcohol) and hydroxypropylcellulose	Oxidation	Oxidation, by adsorbents and surfactants, capacitive deionization

TREATMENT OF HEAVY METALS

- The first step in treating any heavy metal toxicity is to identify the toxic elements and begin the removal process.
- The easiest screening process is a Hair Analysis.
- Additional testing involves the use of chelating drugs along with a 24-hrs urine collection to determine levels of heavy metals.
- Treatment based on the involve the use of metal chelating drugs on intravenous EDTA chelation.

CONCLUSION

- Heavy metals are toxic elements, highly effects to living organisms. So to be taken in permissible limits.
- Heavy metals can be detected by hair analysis, urine sample techniques.
- Consumption of heavy metals too much may leads to toxicity so should be taken in limits.


Thank You