# BHARATHIDASAN UNIVERSITY

## Tiruchirappalli- 620024,

## Tamil Nadu, India

**Programme : M.Sc., Marine Science**

**Course Title : Marine Pollution**

**Course Code : 22MSEC01**

**Unit-II**

**Major Marine Pollutants – Metal Pollution**

**Dr. R. RAJARAM**

**Professor**

**Dept. of Marine Science**

# METALS POLLUTION

## TYPES, SOURCES AND ECOLOGICAL EFFECTS ON MARINE ENVIRONMENT

# INPUT ROUTES

1) Metals are natural constituents of seawater from the erosion of ore-bearing rocks, wind-blown dust, volcanic activity, forest fires and vegetation

2) The nature of input depends on the occurrence of metals and ore-bearing deposits in the drainage area

3) Sedimentation in estuaries traps a large quantity of metals which become absorbed on to sediment particles

4) Regular dredging of shipping channels - heavily contaminated with metals

5) Direct discharge of industrial and other wastes by pipelines

# ATMOSPHERIC INPUTS

1) It may exist as gases (mercury, selenium, boron) or aerosols (most other metals)

2) They are deposited by gas exchange at surface sea or dry deposition (Particle) or precipitation (wet deposition)

3) Air-sea interactions are not a one-way process. Bubbles bursting at the sea surface release sea salt particles to the atmosphere and there is evidence that these particles become enriched with other contaminants during their formation.

# Worldwide emission of trace metals to the atmosphere (thousand t yr-1)

| Metal | Natural source | Anthropogenic source |
|---|---|---|
| Arsenic | 7.8 | 24 |
| Cadmium | 0.96 | 7.3 |
| Copper | 19 | 56 |
| Nickel | 26 | 47 |
| Lead | 19 | 449 |
| Selenium | 0.4 | 1.1 |
| Zinc | 4 | 314 |

# UPTAKE OF METALS

1) Many metals are essential for the living organisms

2) Respiratory pigment haemoglobin found in vertebrates and many invertebrates contains iron

3) The respiratory pigment of many molluscs and higher crustaceans, haemocyanin contains copper

4) The respiratory pigment of tunicates contains vanadium

5) Many enzymes contains zinc

6) Vitamin B12 enzyme contain cobalt

# Metals are biological concern may be divided into three groups

- **Light metals** (sodium, potassium, calcium, and so on) normally transported as mobile cations in aqueous solution
- **Transitional metals** (iron, copper, cobalt, and manganese) which are essential in low concentrations but may toxic in high concentration
- **Metalloids** (mercury, lead, tin, selenium, arsenic) which are generally not required for metabolic activity and are toxic even in low concentration.
- **Transitional metals and metalloids are usually known as heavy metals.**

# SOURCES AND IMPACTS OF HEAVY METALS – GLOBAL SCENARIO

| Heavy metal | Natural sources | Anthropogenic sources | References |
|---|---|---|---|
| Cadmium | 800 to 1,000 mt/year | 8,000 to 10,000 mt/year | Nriagu, 1980; Nriagu 1989; WHO, 1992 |
| Mercury | 2700 – 6000 tonnes / year | 2000 – 3000 tonnes /year | Judith, 2000 |
| Arsenic | 45,480 tonnes/year | 30000 tonnes / year | Chilvers and Peterson, 1987 |
| Copper | 3,25,000 t/year | 7.5 mt/year | Clark, 2001 |
| Lead | 25,000 t / year | 4,50,000 t / year | |

**HEAVY METALS:**

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations and it cannot be degraded or destroyed. A small amount enters our bodies via food, drinking water and air to bioaccumulate in the body to cause dangerous. Eg. Hg, Cd, Pb, As and Cu

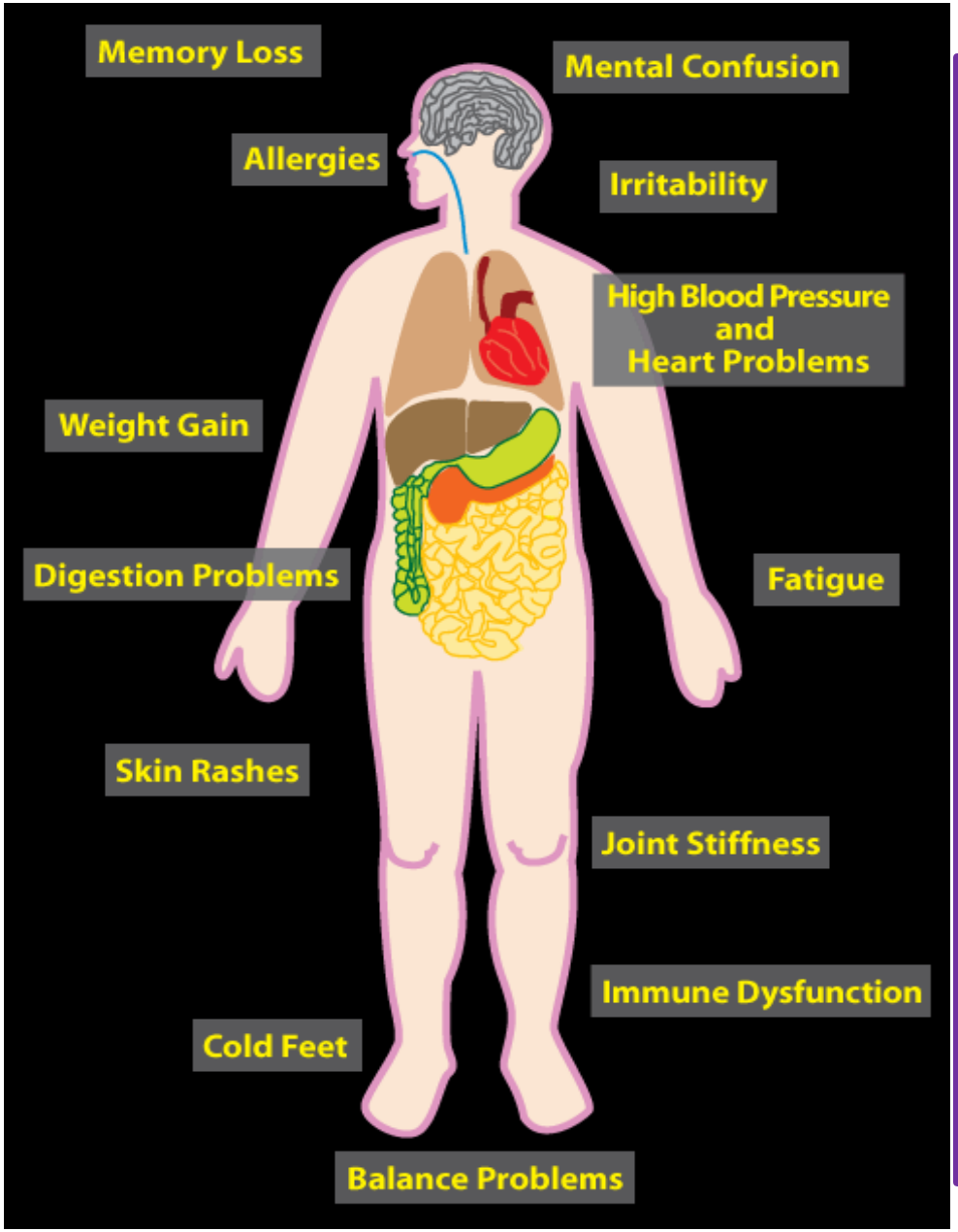
## Natural Sources

- Earth crust
- Volcanic eruption
- Forest fire
- Combustion of fossil fuel

## Anthropogenic Sources

- Pharmaceutical industries
- Paper and pulp
- Agricultural industries
- Biocides and fertilizer industries
- Paint
- Mining
- Chlor-alkali
- Electrical apparatus manufacturing
- Thermal power plants
- Metal processing
- Laboratory usage

# EFFECTS OF HEAVY METALS ON HUMEN BODY




## SYMPTOMS RELATED TO HEAVY METAL POISOING

**A. Psychological, physical and behavior problems**

**B. Collapse the immune/endocrine system**
- Immunosupression and reduced WBC count

**C. Damages the central nerve system**

**D. Cardiovascular system**
- High / Low BP; Blood vessel damage
- Pain in the heart region

**E. Intestine**
- Stomach pains
- Stomach ulcers

**F. Skin problems**
- Dry skin
- Rashes
- Itchy skin

**G. Oral problems**
- Bleeding gums

# ANTHROPOGENIC INPUT OF TOXIC METALS INTO THE ENVIRONMENT

## Source of mercury

- Electrical apparatus
- Chlor-alkali industry
- Paints (antifouling)
- Industrial control instruments
- Dental enamels
- Agricultural biocides
- Catalysts
- Laboratory use
- Pharmaceuticals
- Paper and pulp
- Amalgams

## Source of Cadmium

- Fumes, dust and wastes water from lead and zinc mining and refining
- Rinsing water from electroplating industries
- Iron, steel and non-ferrous metal industries produce dust, fumes, waste water and sludge containing cadmium
- Automobiles tyres containing 20-90ppm Cd
- Phosphate rock contains 100ppm of Cd
- Coal contains 0.25 – 5.0ppm of Cd
- Heating of oil produces 0.3ppm of Cd
- Sewage sludge contains upto 30ppm of Cd

# MERCURY

## SOURCE AND INPUTS TO THE MARINE ENVIRONMENTS:

- The annual world production of mercury in 1971 is 10600 tonnes (Anthropogenic source)

  Natural inputs of mercury are from two sources

  - 3500t yr-1 is derived from weathering of mercury-bearing rocks
  - 25000 to 150,000 t yr-1 is released into the atmosphere as gases from volcanic areas, geothermal vents and earth's crust

- Major source of mercury in coastal waters are river, marine outfalls, and wastes dumped into the sea

- Microbial system in the marine environments converts the inorganic form of mercury into methyl mercury

# INDUSTRIAL SOURCE OF MERCURY

- Electrical apparatus
- Chlor-alkali industry
- Paints (antifouling)
- Industrial control instruments
- Dental enamels
- Agricultural biocides
- Catalysts
- Laboratory use
- Pharmaceuticals
- Paper and pulp
- Amalgams

# TOXICITY OF VARIOUS MERCURY COMPOUNDS IN ALGAE AND INVERTEBRATES

1. Methyl mercuric chloride
2. Ethyl mercuric chloride
3. n – Propyl mercuric chloride
4. n- Butyl mercuric chloride
5. n- Amyl mercuric chloride
6. Isopropyl mercuric chloride
7. Isoamyl mercuric chloride
8. Phenyl mercuric chloride
9. Phenyl mercuric iodide
10. Mercuric iodide
11. Mercuric chloride

# MERCURY IN FISH

1) Many species of fish in ocean contains 0.15ppm which is lower than mercury in mollusks

2) Most of the fishes are carnivores and at the end of food-chain and their diet contains high level of mercury resulting from bioaccumulation and biomagnifications

3) Some fishes are active swimmer – mouth open – continuous exchange of water

# MINAMATA DISEASE

- First report 1953 – 1956
- Vinyl chloride factory in Minamata bay in Japan – Mercury chloride is used as a catalyst for the manufacture of vinyl chloride
- Minamata bay sediment 200ppm; plankton 5ppm; bivalve 10-39ppm; fish 10-55ppm
- 2000 cases recognized, 43 died, 700 became permanently disabled
- Second outbreak of Hg poisoning in Japan occurred among the fisherman living near the mouth of Agamo river in 1965
- This is caused by the contamination of fish by Hg from the industrial effluent from the factory 60kms upstreams

# Symptoms:

Methyl Hg is more dangerous than the inorganic Hg to humen because it can't be excreted (Methylating Bacteria)

Loss of neuromuscular co-ordination

Brain damage

Crippling effect

CNS damage

Hemorrhage

# PUBLIC HEALTH STANDARDS:

**WHO – Hg in food is 0.2mg methyl Hg: 0.3mg of total mercury per week**

## Sea food standards

- **0.5ppb – US and Canada**
- **0.7ppb in Italy**
- **1.0ppb in Germany, japan, Switzerland**
- **1.5ppb in Norway**

# MERCURY POISONING – Minamatta disease

# MERCURY POISONING - Crippling effect

# CADMIUM POLLUTION

## SOURCES AND INPUT

- It is widely distributed in the earth crust
- Total world production is about 150, 000 to 180, 000t $yr^{-1}$
- Total world ocean input of Cd is about 8000 t $yr^{-1}$ (half of it is man made activities)
- 2900 t $yr^{-1}$ is deposited in sediments
- Cd content of sea is increasing slowly
- Fumes, dust and wastes water from lead and zinc mining and refining

- Rinsing water from electroplating with 100-500ppm
- Iron, steel and non-ferrous metal industries produce dust, fumes, wastewater and sludge containing cadmium
- Automobiles tyres containing 20-90ppm Cd
- Phosphate rock contains 100ppm of Cd
- Coal contains 0.25 – 5.0ppm of Cd
- Heating of oil produces 0.3ppm of Cd
- Sewage sludge contains upto 30ppm of Cd

# CADMIUM IN MARINE ORGANISMS

- It is not an essential element
- It enhances phytoplankton photosynthesis and growth
- Fishes and mammals contains low concentration of Cd (Detoxify by the production of metallothionein)
- Zooplankton accumulates more amount of Cd
- Molluscs especially bivalves accumulates up to 2000ppm

# ITAI-ITAI DISEASE

- ***Itai-itai disease*** **was caused by cadmium poisoning due to mining in Toyama Prefecture**
- **The Itai-itai disease occurred in Toyama around 1950 in Japan**
- **literally: "ouch-ouch" disease**
- **Regular mining for silver, lead, copper, and zinc began after 2nd world war**
- **Subsequently increased the pollution of the Jinzu River and its tributaries**
- **The river was used mainly for irrigation of rice fields, but also for drinking water, washing, fishing, and other uses by downstream populations**

- **Due to the cadmium poisoning, the fish in the river started to die, and the rice irrigated with river water did not grow well.**

- **The cadmium and other heavy metals accumulated at the bottom of the river**

- **The rice absorbed heavy metals, especially the cadmium. The cadmium accumulated in the people eating contaminated rice.**

- **Medical tests started in the 1940s and 1950s, searching for the cause of the disease that determining the Mitsui Mining and Smelting's Kamioka Mining Station caused the cadmium pollution**

- **In 1968 the Ministry of Health and Welfare issued a statement about the symptoms of *itai-itai* disease caused by the cadmium poisoning.**

# Symptoms

a) Severe pain in the joints and spine

b) Weak and brittle bones.

c) Spinal and leg pain is common

d) Bone deformities and bone weakens

e) Coughing, anemia, and kidney failure, leading to death

f) A marked prevalence in older, postmenopausal women has been observed.

# Itai-Itai disease

- Caused from cadmium mining waste dumped in rivers and then used for irrigation of crops
- Japan, 1950
- "Ouch-ouch" disease; extremely painful; attacks bones

# CADMIUM POISONING – Itai itai Disease

Chronic exposure of cadmium affects the lungs and kidneys. Itai-itai disease was the documented case of mass cadmium poisoning in Toyama region, Japan (Jintsu river).

## Symptoms:

- severe pains caused in the joints and spine.
- Softening of the bones (Brittle bone) and kidney failure.
- Coughing and anemia,
- adversely affects reproduction and survival.
- finally it leading to death.

Children with Congenital Minamata Disease due to intrauterine

# PUBLIC HEALTH STANDARD

- **Drinking water - maximum contaminant level for cadmium in drinking water is 0.005 mg/L. (ATSDR, 1999)**

- **Soil – EPA biosolids rule states that the ceiling for the amount of cadmium that can be applied to land is 85 mg/kg fill material (NTP 2004).**

- **Food – Reference dose is $1 \times 10^{-3}$ mg/kg/day (ATSDR 1999).**

- **Water - Reference dose for human exposure is $5 \times 10^{-4}$ mg/kg/day.**

- **Tolerable weekly intake for cadmium at 7µg/kg/body weight/week**

- **Maximum limit of cadmium in bottled water: 0.005 mg/L.**

# COPPER POLLUTION

## SOURCE AND INPUTS TO THE SEA

- Natural input from erosion and mineralization of rock is about 325000 t $yr^{-1}$
- Input from industrial activity is about 7.5 million t $yr^{-1}$
- Electrical equipment
- Alloys
- Chemical catalyst
- Antifouling paints (500g $l^{-1}$
- Algicide
- Wood preservatives

# CU IN MARINE ORGANISMS

- Cu is an essential element for animals and high concentration is found in decapod crustaceans, gastropods, cephalopods and respiratory pigment of haemocyanin
- Excess copper is stored in liver – 4800ppm
- Oyster acquire very high concentration of Cu in leucocytes.
- Marlin - 0.4ppm in muscle; 4.6ppm in liver
- Polychaete – 1000ppm
- Contaminated sediment – 2148ppm

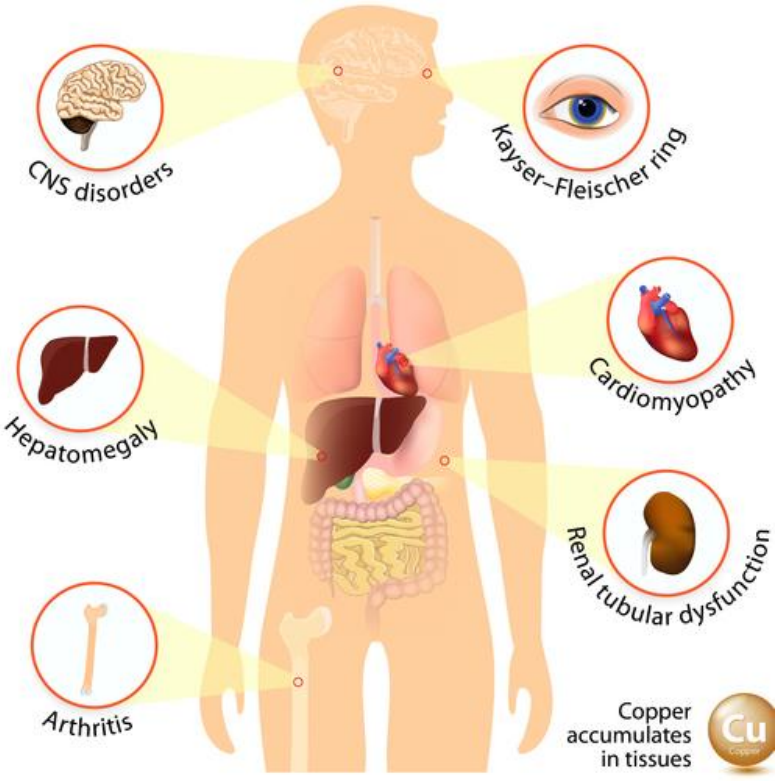
# WILSON'S DISEASE (Cu)

Wilson's disease is a rare inherited disorder that causes copper to accumulate in your liver, brain and other vital organs.

Most people with Wilson's disease are diagnosed between the ages of 5 and 35, but it can affect younger and older people, as well.

## Symptoms

- Fatigue, lack of appetite or abdominal pain
- A yellowing of the skin and the whites of the eye
- Golden-brown eye discoloration (Kayser-Fleischer rings)
- Fluid buildup in the legs or abdomen
- Problems with speech, swallowing or physical coordinatio
- Uncontrolled movements or muscle stiffness




## Complications

- **Liver cirrhosis**
- **Liver failure**
- **Kidney problems**
- **Persistent neurological problems**

# LEAD POLLUTION

## SOURCES AND INPUT

- The total world production of Pb is 43million t $yr^{-1}$
- Natural input – 25000 t $yr^{-1}$
- Anthropogenic source – 450 000t $yr^{-1}$
- Automobiles and sewage sludge
- Natural concentration is 0.015 m g/l in sea water
- The total lead discharge in water is 3.8 million kg.
- Car batteries.
- Cosmetics e.g. kohl, surina Drugs.
- Paint chips.
- Toys.
- Old run-down buildings.

- **Contaminated foods such as fruits and vegetables grown in contaminated soils.**
- **Water from lead pipes, fixtures or valves.**
- **Stained glass windows.**
- **Playground soil.**
- **Household dust.**
- **Electrical wiring.**
- **Soldering.**
- **Heroin.**

# Symptoms of lead poisoning

## Symptoms of lead poisoning

- Abdominal pain,
- Muscular weakness and fatigue,
- Constipation, and headache.

**Severe exposure:**

- Nervous system disorders,
- High blood pressure,
- Finally death

Abdominal pain

Fatigue

Lead Poisoning

Head ache

# THANK YOU