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Trace Metals in the Aquatic Environment and its Effect on Aquatic Life and Human Body

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Abstract: ***The contamination of natural waters by heavy metals negatively affects aquatic biota and poses considerable environmental risks and concerns. One of the peculiar features of fish and fishery products are that they concentrate several trace elements such as Ag, Hg, Pb, Cd, Cr, Cu and Zn at sometimes very high concentrations. Some metal like copper (Cu), Iron (Fe) and zinc (Zn) are essential for normal metabolic and physiological functions of fish while other metals like mercury (Hg), lead (Pb) and cadmium (Cd) have no known biological role. Elevated concentrations of such heavy metals, especially cadmium, not only results in bio - magnification, as they constitute a major food source for top predator species, but also pose a health hazard to the human population that consume the species. Monitoring programmes and research on bioaccumulation of heavy metals in aquatic environments samples have become widely important due to 2 concerns over accumulation and toxic effects in aquatic organisms and to humans through the food chain. Contaminants can persist for many years in sediments in both freshwater and marine systems where they hold the potential to affect human health and the environment. Recently, import regulations have increased on heavy - metal residues in fish and other cephalopod products. These include arsenic, tin, cadmium, lead, chromium, mercury and nickel. Member States are required to implement a monitoring system to check the level of contamination of fish and fishery products, produced both domestically and imported.***

Keywords: Bioaccumulation, Pollution, Heavy Metals, Environment.

Trace metals play an important role in the aquatic ecosystem. Heavy metals may enter aquatic systems from different natural and anthropogenic (human activities) sources, including industrial or domestic waste water, application of pesticides and inorganic fertilizers, storm runoff, leaching from landfills, shipping and harbour activities, geological weathering of the earth crust and atmospheric deposition (Connell et al., 1999; Franca et al., 2005).

In the last decades, contamination of aquatic systems by heavy metals has become a global problem. The contamination of natural waters by heavy metals negatively affects aquatic biota and poses considerable environmental risks and concerns (Cajaraville et al., 2000; Ravera, 2001). Contaminants can persist for many years in sediments in both freshwater and marine ecosystems where they hold the potential to affect the human health and the environment. Monitoring programmes and research on heavy metals in aquatic environments, samples have become widely important due to concerns over accumulation and toxic effects in aquatic organisms and to humans through the food chain (Otchere, 2003).

The term 'trace metal' is used to designate the elements, which occur in small concentrations (<100 ppm) in natural biological systems. There are both essential and non - essential trace metals. It is well known that copper (Cu), nickel (Ni), cobalt (Co), zinc (Zn), chromium (Cr), iron (Fe) and manganese (Mn) are essential to life (Mertz, 1981) and known as essential trace metals. The elements aluminum (AI), antimony (Sb), mercury (Hg), cadmium (Cd), germanium (Ge), vanadium (V), silicon (Si), rubidium (Rb), silver (Ag), gold (Au), lead (Pb), titanium (Ti) etc are believed to be acquired by animal tissue from environmental contaminants, due to interaction of organism with the environment. These elements are usually concentrated in different organs unevenly and are termed as non - essential elements. Essential metals function either as an electron donor system or as ligands in complex enzymatic compounds in animals.

Since essential elements are used by the organisms only in trace amounts, their enrichment in the organisms does not exceed the level which allows the enzyme system to function without interference (Presley, 1997). However, if the heavy metal concentration at the source of supply is too high, the homeostatic mechanism ceases to function and the essential heavy metals act either in acutely or chronically toxic manner. Thus, in the event of extended bioaccumulation of heavy metals, the organism may be affected. Trace metals in the aquatic environment and its effect on aquatic life and human body.

Sources of heavy metals

Trace metals are introduced in the environment from both natural sources and human activity (Penrose et al., 1975; Phillips et al., 1982; Martin andScanes, 1996; Presley, 1997). A large number of heavy metals may be contributed by corrosion of metal pipes, smelting, refining, etc. Weathering is a natural source of dissolved and particulate trace metals. Geological weathering of rocks produces the clays and other minerals that make up the bulk of detritus sediments as well as the bulk of dissolved metals in seawater. Volcanic activity, either on land or in the sea, is another natural source of metals. Emissions of heavy metals to the environment occur via a wide range of processes and pathways, including to the air (e. g. during combustion, extraction and processing), to surface waters (via runoff and releases from storage and transport) and to the soil (and hence into groundwaters and crops). Sources of some Heavy metals in water environment showed in table 1. (Yanli Wang et, al.*2*022).

The environmental impact of a metal depends less on its source than on itsbehaviour, including mobility, transport, transfer and biological uptake, depends strongly on the chemical and physical form of the metal. The toxicity of a metal is mainly determined by its ionic size, electron affinity, electro negativity, stability, solubility and its inherent capacity is to affect adversely on any biological activity (Wittmann, 1974). The heavy metals have highaffinities for ligands containing sulphur and nitrogen, and hence are bound easily to organic molecules such as proteins, enzymes etc (Richardson, 1980).

Many of the heavy metals are toxic to organisms at low concentrations. Concentrations of essential elements in organisms are normally homeostatically - controlled, with uptake from the environment regulated according to nutritional demand. Effects on the organisms are manifest when this regulation mechanism breaks down as a result of either insufficient (deficiency) or excess (toxicity) metal (Duffus, 2002). Toxic metals change the biological structures and systems into inflexible and irreversible conformation leading to deformity in the body and finally death (Kudesia, 1980).

Table 1: Sources of some Heavy metals in water environment

Heavy Metals	Source
Pb	Paint, pesticide, smoking, automobile exhaust, coal, combustion etc.
Hg	Mineral resources, fossil fuels, ores, pesticides, batteries, paper industry.
Cd	Steel and plastics industry, cooling tower, metal electroplating and coating operation, nickel cadmium battery, cadmium film, solar cell, pigments, galvanized pipes, welding, fertilizers and nuclear emission device.
Cr	Industrial waste water discharged into environment, cooling tower blowdown, metal electroplating and coating operation
Cu	Pesticide industry, mining, metal pipeline, chemical industry.
Zn	Brass mapping, wood pulp production, grinding and newsprint production, iron and steel plants with zinc lines, zinc and brass metal products, refineries and pipelines.
Se	Waterloss, rock weathering, rainfall and decomposition of organisms, combustion of coal and oil, agriculture irrigation use of phosphate pesticides and fertilizers.
Ni	Battery manufacturing, alloy production, Zinc base casting, printing, electroplating, silver refinery.

Toxic effects of heavy metals on aquatic organisms

Heavy metals in water enter aquatic organisms in three ways. First, aquatic animals absorb heavy metal ions in water through gill tissues and then transport them to various tissues of the body. Second, aquatic animals absorb heavy metals in to their bodies by ingesting food contaminated with heavy metals. Third, heavy metals enter the bodies of aquatic animals by osmotic exchange through subcutaneous absorption. (long et, al., 2016) Table 2. shows toxicological effects of heavy metal pollution on organisms at different levels.

Some heavy metals entering aquatic animals can promote the growth, metabolism and enzyme activity of aquatic animals within an appropriate concentration range. However, with the extension of exposure time, due to accumulation effect of metal ions on aquatic animals when its concentration reaches a certain threshold, it produces a series of toxicological effects on the growth, physiology and biochemistry, genetic gene expression, behaviour, metabolism and other processes of aquatic animals.

Moreover the potential risks of heavy metals to different kinds of aquatic animals are also different. Du et al 2013 compared the sensitivity of marine vertebrates and invertebrates to eight kinds of heavy metals and the acute ecological risk of different metals, indicating that the ecological risk of heavy heavy metals to crustaceans is greater than fish. Research showed that aquatic animals of benthic oligochaetes are more sensitive to heavy metal pollution followed by leeches, gastropods and insects. The enrichment of heavy metals by aquatic animals is related to specific factors such as age, geographical distribution, season, species differences and the form of heavy metals. Moreover the distribution of different kinds of heavy metals in different tissues of aquatic animals is also different, so it will cause different Eco toxicological effects on aquatic animals. (Yanli Wang et, al.2022)

Table 2: Shows Potential Toxicological Effects of Heavy Metals

Heavy metal	Potential toxic effects of heavy metals
Pb	Anemia, cancer, kidney disease, neurological impairment, mental retardation, mental impairment and behavioural problems in children.
Hg	Damage to the immunity of the renal reproductive system, damage to th blood, cardiovascular and respiratory systems and the brain.
Cd	Renal cancer damage, bronchiolitis, chronic obstructive pulmonary disease, emphysema, fibrotic bone damage.
Cr	Severe diarrhoea, vomiting, pulmonary congestion, liver and kidney damage
Cu	Increased blood pressure and breathing, kidney and liver damage, convulsions, spasms, vomiting.
Zn	Gastric nausea, skin irritation spasms, vomiting and anemia.
Se	Gastrointestinal discomfort, hair and nail loss, fatigue, cardiac arrhythmia and nerve injuries.
Ni	Dry coughing, cancers of bone, nose and lung, shortness of breath, chest tightness, chest pain, nausea, vomiting, dizziness and headache.

Mercury:

Contamination of marine organisms with toxic metals such as mercury (Hg) is of ecological and health concern worldwide (Goldberg, 1995). The presence and behavior of Hg in aquatic systems are of great interest and importance since it is the only heavy metal which bioaccumulates and biomagnifies through all levels of the aquatic food chain (Lindqvist et al., 1991). Mercury has not necessary function in any living organism and is considered as a non - essential metal, is among the most toxic elements to man and many higher animals (Steinnes, 1995).

There are three forms of Hg and among these the most toxic one is the organic form, methyl mercury. Methyl mercury is microbiologically transformed from inorganic mercury when it reaches aquatic environments, in water bodies or in soils (Zahir et al., 2005). Inorganic - and organic mercury is toxic to the human body in different ways, affecting different organs in different ways. Inorganic mercury can cause neurological and psychological symptoms, such as tremor, changes in personality, restlessness, anxiety, sleep disturbance and depression. These symptoms are however reversible after ending of exposure to inorganic mercury. Inorganic mercury is also an allergen, which may cause contact eczema. The kidneys are the organs that accumulate the highest levels of Hg when compared to brain and liver. This can cause kidney damage which is reversible after the exposure has stopped (Zahir et al., 2005).

Methyl mercury, toxicity is not reversible as it is with inorganic mercury. Organic mercury affects the nervous system and the main symptoms of methyl mercury poisoning relate to damage of the nervous system. The earliest symptoms of poisoning are parestesias and numbness in the hands and feet. Later symptoms are coordination difficulties and concentric constriction of the visual field (Jarup, 2003). Other symptoms are memory loss, shortfall in attention and Alzheimer's disease like dementia (Zahir et al., 2005). Hock et al. (1998) conducted a study on whether environmental factors may influence the risk of getting Alzheimer's disease and found that Alzheime's disease patients had a two - fold higher blood - mercury level than the control group and that early onset Alzheimer's disease patients, blood - mercury levels where three - fold higher than the control group. Exposure of the fetus of humans to mercury can also cause late development of speech, late walking, memory shortfall in attention and autism. The general human population is primarily exposed to mercury via food, where fish is the major source of methyl mercury exposure (Jarup, 2003).

Mercury has caused more problems to the fish consumed than any other inorganic contaminant. In extreme cases, consumption of mercury - tainted fish has led to the onset of a serious neurological disease, termed Minamata disease. The first reported human poisoning by Hg in seafoods occurred in Japan, between 1953 and 1964, which is known as 'Minamata' disease (Nitta, 1972). Victims of the disease are diagnosed as having a degeneration of their nervous systems. Numbness occurs in their limbs and lips. Their speech becomes slurred, and their vision constrict. Some people have serious brain damage, while others lapse into unconsciousness or suffer from involuntary movements. Furthermore, some victims are thought to be crazy when they begin to uncontrollably shout.

The discharge of wastes containing mercury from chlor - alkali plants, Rayon factory and paper industry causes Hg poisoning, which is evident in Chaliyar River in Kerala, Rushikulya River in Orissa and Thane creek near Bombay. Hg poisoning results in chromosomal damages resulting from the combination of mercurial with - SH groups of enzymes and - NH2 groups of amino acids (Bloom, 1992; Bustamante, 2006).

Cadmium:

Cadmium (Cd) is regarded as one of the most toxic metals. The poisoning implicated by Cd containing food is known as 'itai - itai' disease in accordance with the patient's shrieks resulting from painful skeletal deformities. 'itai - itai' disease was first reported in Jintsu River, Toyama Prefecturor, Japan (Friberg et al., 1974). The disease was characterized by kidney malfunction; drop in the phosphate level of the blood serum and loss of minerals from the bones. Anthropogenic sources of Cd include the mining and minerals processing industries, Zn smelting, paint and plastic industry, effluent from Ni/Cd batteries, urban runoff due to the elevated Cd concentrations in phosphate fertilizers etc. Cadmium has been found to be toxic to fish and other aquatic organisms (Rao and Saxena, 1981; Woodworth and Pascoe, 1982). The effect of Cd toxicity in man caused kidney damage (Friberg, et al., 1986; Herber et al., 1988) and pains in bones. Cd also has mutagenic, carcinogenic and teratogenic effects (Fischer, 1987; Friberget al., 1986, Kazantzis, 1987, Heinrich, 1988).

Cadmium compounds are currently mainly used in re - chargeable Nickel - Cadmium batteries. Cadmium emissions have increased dramatically during the 20th century, one reason being that cadmium - containing products are rarely re - cycled, but often dumped together with household waste. Cigarette smoking is a major source of cadmium exposure. In non - smokers, food is the most important source of cadmium exposure. Recent data indicate that adverse health effects of cadmium exposure may occur at lower exposure levels than previously anticipated, primarily in the form of kidney damage but possibly also bone effects and fractures. Therefore, measures should be taken to reduce cadmium exposure in the general population in order to minimize the risk of adverse health effects.

Lead:

Lead (Pb) is defined by the United States Environmental Protection Agency (USEPA) as potentially hazardous to most forms of life, and is considered toxic and relatively accessible to aquatic organisms (USEPA, 1986). Lead is considered as a protoplasmic poison, which is a cumulative, slow acting and subtle. The Greek poet - physician Nicander described the disease known as plumbism, which is caused by acute Pb poisoning. Lead is introduced into the environment by various industries such as storage batteries, production of chemicals including paints, gasoline additives and various metal products (eg sheet, pipes). Lead is emitted in large amounts from municipalities, through incineration of waste products. High levels of Pb have been found in urban runoff. Because Pb is used as an anti - knocking agent in gasoline in many countries, elevated levels of Pb found in urban air and by precipitation it will be carried to the nearby water bodies.

Lead is bioaccumulated by benthic bacteria, freshwater plants, invertebrates and fish. The chronic effect of Pb on human includes neurological disorders, especially in the foetus and in children. This can lead to behavioral changes and impaired performance in IQ tests (Lansdown, 1986; Needleman, 1987).

Lead has been used for at last 5000 years, early applications including building materials, pigments for glazing ceramics, and pipes for transporting water. The symptoms of acute lead poisoning are headache, irritability, abdominal pain and various symptoms related to the nervous system. Lead encephalopathy, the affected person may suffer from acute psychosis, confusion and reduced consciousness. People who have been exposed to lead for a long time may suffer from memory deterioration, prolonged reaction time and reduced ability to understand. Individuals with average blood lead levels under 3µmol/1 may show signs of peripheral nerve symptoms with reduced nerve conduction velocity and reduced dermal sensibility. If the neuropathy is severe the lesion may be permanent. The classical picture includes a dark blue lead sulphide line at the gingival margin. In less serious cases, the most obvious sign of lead poisioning is disturbance of haemoglobin synthesis, and long term lead exposure may lead to anaemia. Recent research has shown the long - term low level exposure in children may lead to diminished intellectual capacity. (Yanli Wang et, al.2022)

Copper

Copper (Cu) is an essential trace element for the fixation of Fe in hemoglobin and is net a potent liver toxin except in certain case of genetic defects resulting in the inability to excrete Cu, the primary homeostatic mechanism, for instance Wilson's disease. Copper in ionic form is found to be toxic and inhibits photosynthesis and affect the growth of unicellular algae (Nielson and Anderson, 1970). Cu in excessive amounts causes haemolysis, hepatotoxic and nephrotoxic effects. The phenomenon of green - sick oysters is influenced by high content of Cu in the environmental water. The effluents from Cu refineries, pesticide and fungicide manufacturing industries bring Cu to the aquatic systems. In Taiwan, Cu pollution due to the discharges from the local Cu recycling operation has been reported and this has caused serious toxicity in green oysters (Hung et al., 1989). The highest level of Cu in the oysters collected from the polluted area was 4400 ppm (Hung and Han, 1991). Thus, higher level of Cu in the environment or marine organisms adversely affects quality and fishery and can cause great economic loss.

Zinc:

Zinc (Zn) is widely used in modern society, most commonly to coat or galvanise iron to prevent corrosion. It is also mixed with other metals to form alloys like brass. Particles released from vehicle tyres and brake linings are a major source of zinc in the environment (WHO, 2001). Zinc is an essential nutrient for the human body and has an importance for health (Hotz et al., 2003). Zinc acts as a catalytic or structural component in many enzymes that are involved in energy metabolism and in transcription and translation of RNA (Moolenaar, 1998). Zinc also has a prominent role in determining the outcomeof pregnancies and supporting neurobehavioral development (Hotz et al., 2003). However, like other metals, it can be toxic in high concentrations. Although uncommon, gastrointestinal distress and diarrhoea have been reported following ingestion of beverages standing in galvanized cans or from use of galvanised utensils (WHO, 2001). Other symptoms of Zn toxicity are slow reflexes, shakes, paralyzation of extremities, anemia, metabolic disorder, terratogenic effects and increased mortality (Klaassen, 1996).

Iron:

Iron, (Fe) one of the most abundant metals on earth, is essential to most life forms and to normal human physiology. Iron is an integral part of many proteins and enzymes that maintain good health (Institute of Medicine, 2001). In humans, iron is an essential component of proteins involved in oxygen transport (Dallman, 1986). It is also essential for the regulation of cell growth and differentiation. A deficiency of Fe limits oxygen delivery to cells, resulting in fatigue, poor work performance, and decreased immunity. On the other hand, excess amounts of iron in human can result in toxicity and even death (Corbett, 1995). There is considerable potential for iron toxicity, very little amount of iron is excreted from the body. Thus, iron can accumulate in body tissues and organs when normal storage sites are full. For example, people with hemachromatosis are at risk of developing iron toxicity because of their high iron stores. Symptoms of Alzheimer’s and Parkinson’s disease may also be iron - related (Cornell, 1999).

Manganese:

Manganese (Mn) is one of the abundant elements in the earth's crust and is widely distributed in soils, sediments, rocks, water, and biological materials. A rough estimate of the average concentration of manganese in the earth's crust is about 1000 mg/kg (NAS/NRC, 1973). Manganese is quite significant in the marine environment because of its reactivity. It is present in appreciable amounts in marine sediments. Mn affects the trace metal distribution in the marine environment as a result of adsorption on manganese nodules (Morgan and Stumm, 1964; Murray, 1975; Cronan, 1980; Manheim, 1986). The geochemical distribution of Mn in seawater is quite irratic and is influenced mostly by its redox potential. Mn toxicity in humans is characterized by a severe psychiatric disorder resembling Schizophrenia, followed by a permanent crippling neurological disorder clinically similar to Parkinson's disease (Hurley and Keen, 1987).

Chromium

Chromium (Cr) is one of the least toxic of the trace elements and the mammalian body can tolerate 100 to 200 times its total body content of Cr without harmful effects. Chromium is essential for human body for glucose tolerance (Prufulla et al., 2001).

Nickel

Nickel (Ni) is a nutritionally essential trace metal for at least several animal species, micro - organisms and plants, and therefore either deficiency or toxicity symptoms can occur when, respectively, too little or too much Nickel is taken up. Although a number of cellular effects of nickel have been documented, a deficiency state in humans has not been described (Benco, 1983; Klaassen, 1996; Barceloux, 1999; Uthus et al., 1996; Scott Fordsmand, 1997). Nickel and nickel compounds have been used in many industrial andcommercial purposes, and the progress of industrialization has led to increased emission of pollutants into ecosystems. Although Ni is omnipresent and is vital for the function of many organisms, concentrations in some areas from both anthropogenic release and naturally varying levels may be toxic to living.

Nickel is considered to be a normal constituent of the diet and its compounds are generally recognized as safe when used as a direct ingredient in human food. Nowadays it is thought that Ni plays a role in hormone, lipid and cell membrane metabolism, as well as activating enzymes associated with the glucose breakdown and use (Acu - Cell, 2007). Nickel levels in foodstuffs generally range from less than 0.1 mg/kg to 0.5 mg/kg. A few foods may have obtained Ni during the manufacturing process but in most it apparently occurred naturally.

Many other diseases like Bush Sickness, Black foot diseases, Genavelgum diseases, Wilson's diseases, and White muscle disease are reported as manifestations of heavy metal poisoning. It is in light of the above, monitoring of heavy metals in marine fishes and shellfishes assumes importance from the view point of consumer safety. Higher levels of Cd and other toxic metals were observed in cephalopods, especially in many squid and cuttlefish products imported to Italy (Cantoni, 1986) and in the cuttlefish products exported from India. Some of the frozen cephalopod products (mainly squid and cuttlefish) were detained or rejected in the late 80's, owing to higher levels of Cd. Recently, in 2011 some cuttlefish products exported from Veraval and India, also had high Cd concentration. In 2004 - 05, there were four rejections of export consignments sent from India to European Union countries on amount of high level of cadmium in squids (L. Narasimha Murthy et al., 2009). In the first half of 2004, more than one - third of total Chinese seafood rejections in the U. S. was on account of high levels of cadmium, mercury and other heavy metals. Heavymetal concentrations are often determined by variables such as water contamination, mining activity and effluent treatment activities in the fishing region (Kulkarni 2005).
The Provisional Maximum Tolerable Limit for Daily Intake (PMTDI) of the heavy metals for human consumption as permitted under the guidelines as prescribed by JECFA (1982, 1983, 1993 and 2000)

Table 3: Tolerable Daily Intake of Heavy Metals by Human as Prescribed by JECFA (2000)
Heavy metals Provisional Maximum Tolerable Daily Intake (PMTDI) (mg/kg)

Heavy metals	
Pb	0.025
Cr	0.1 - 1.2
Co	0.005 - 1.8
Ni	0.1 - 0.3
Hg	0.025
Mg	250 - 380
Fe	0.8
Zn	0.3 - 1.0
Cu	0.05 - 0.5
Mn	0.4 - 10

Presence of high levels of cadmium in the economically important class of cephalopods has caused serious concern in the processing and export industry. In the light of these observations, investigations were carried out by Lakshmanan (1988a, 1989) and Lakshmanan and Stephen (1993) in seafood products particularly in cephalopods from the west coast of India. The survey indicated that fishes in general, had only lower levels of Cd and other trace metals compared to squid and cuttlefish. The cephalopods showed a unique phenomenon of bioaccumulation of Cd and other trace metals in different organs of the body. Cephalopods being voracious fish eaters depend on a wide range of marine animals particularly crustaceans, molluscs and fishes and hence there exist the possibility of bioaccumulation of pollutants through food chain.

The presence of these toxic chemicals/metals in aquatics has to be monitored and sources ascertained. To meet the global challenges in seafood trade, we need to ensure that our fish products are both safe and comply with international quality requirements and standards. Recently, import regulations have increased on heavy metal residues in fish. These include arsenic, tin, cadmium, lead, chromium, mercury and nickel. The EU limits levels of heavy metals and other environmental contaminants that can be present in fish and sea food products.

In general, levels are disallowed if dietary intake would likely exceed acceptable daily or weekly intake for humans (Directive 91/493/EC). Member States are required to implement a monitoring system to check the level of contamination of fish and fishery products, produced both domestically and imported. Specifically, the EU has published cadmium content was 1mg/kg in cephalopods (Regulation 2001/466/EC). Since 2004, heavy metal residue has replaced antibiotic and microbiological contamination as the biggest concern of the future.

In the human body, the metallic toxicants attack the proteins notably the enzymes and their toxic effects are cumulative and cause slow poisoning of the system over a period of time. Heavy metals have been implicated in the upsurge of liver and kidney diseases, and is believed to be responsible for a high proportion of mortality caused by kidney and liver morbidity, pains in bones, mutagenic, carcinogenic and teratogenic effects neurological diorders, especially in the foetus and in the children which can lead to behavioural changes and impaired performance in IO tests) Friedberg et al., 197

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