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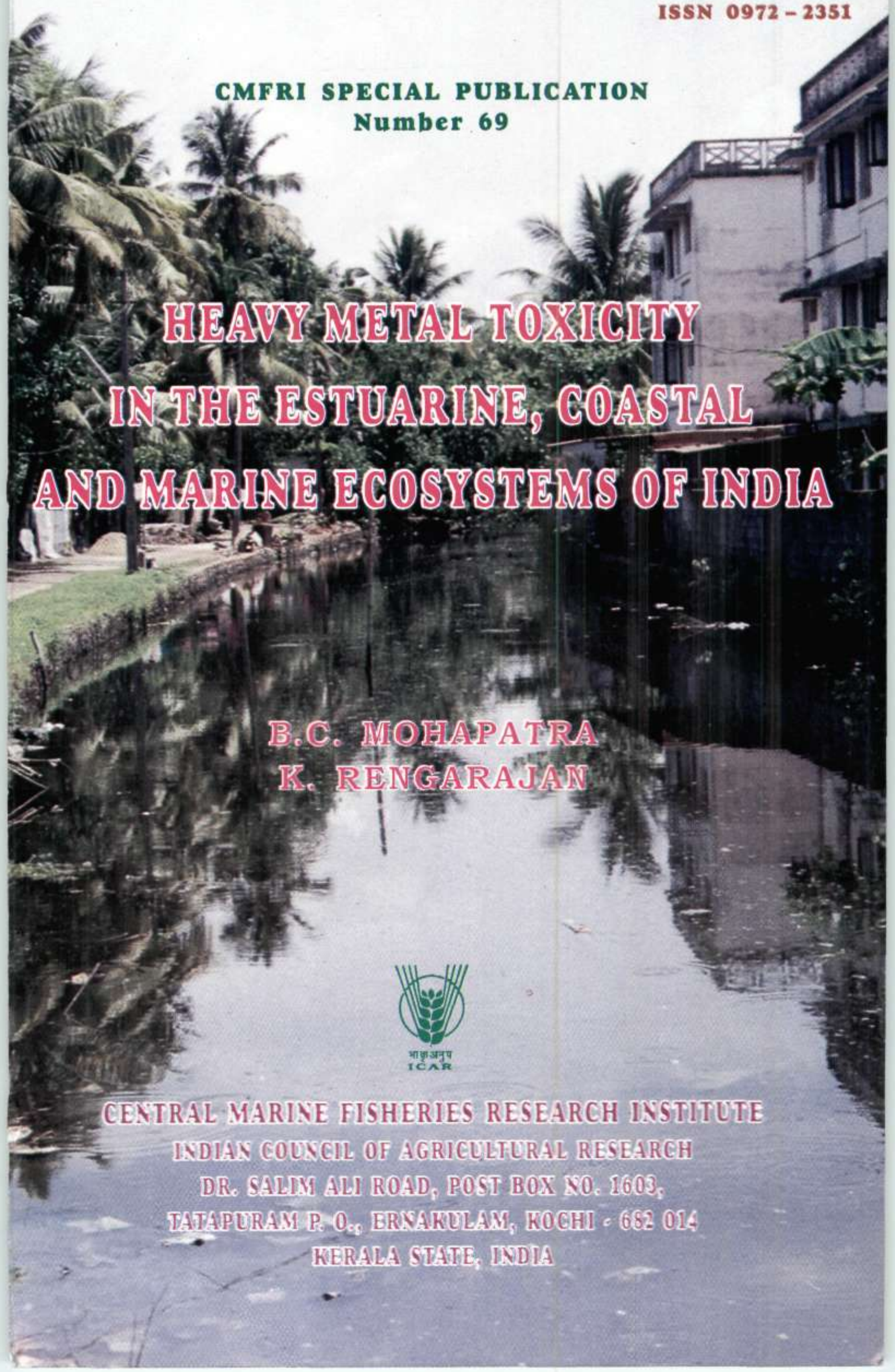

HEAVY METAL TOXICITY IN THE ESTUARINE, COASTAL AND MARINE ECOSYSTEMS OF INDIA

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Front Cover : A severely polluted canal (Sewage) in Kochi city.

Back Cover : The waste water from the Sewage Treatment Plant enters into a polluted backwater area in Kochi.

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PREFACE

Mother nature has provided immense natural resources for human beings who worship them. Water is one such natural resources which is a basic requirement for man, without which no life can exist on Earth.

The oceans and seas provide immense amount of both living and non-living marine wealth. But now, due to scientific, technological and industrial advancements, the seas and oceans are regarded as a vast cesspool with an infinite capacity to absorb natural and man-made pollutants. Sufficient reports are available in recent years to understand that there are definite limits to man's abuse of the oceans and in particular many enclosed, semi-enclosed seas and coastal areas. The deleterious effects of pollutants including heavy metals on living resources are much more evident in the estuarine and coastal areas. These ecosystems particularly the estuaries serve as the important feeding and nursery grounds and also "passage zone" for a large number of commercially exploitable and cultivable aquatic organisms. We are well aware that knowingly or unknowingly our coastal environments are getting polluted resulting a great concern on our marine wealth. Already many coastal areas have become either unproductive or unharvestable for a variety of finfish, shellfish and other marine living resources due to indiscriminate entry of domestic and industrial pollutants through the dumping of wastes. This needs urgently a thorough knowledge of the pollutants, their entry, source, nature of toxicity on biota, monitoring of the ecosystem, remedial measures and management, legislation, etc. to save the environment. Many countries including India have already promulgated legislations on effluent treatments and pollution controls, and established Pollution Control Boards / Agencies by their Government.

The research investigations on pollution, particularly in coastal and estuarine environments are recent ones. Hence, the information available is fragmentary and scattered. In this book, the authors have consolidated and correlated the available data in the field of heavy metal pollution and its level in and around the Indian Coast. This book with its comprehensive expressions will be of great use as a practical guide to the researchers, students and planners for getting some idea regarding the *status quo* of heavy metals in the coastal environments of India.

I appreciate the efforts of the authors and I record my thanks to Dr. K. Rengarajan for editing this book.

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Cochin - 14,
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1

INTRODUCTION

The term "metal" designates an element which is good conductor of electricity and whose electric resistance is directly proportional to the absolute temperature (Wittmann, 1979). In addition to this distinctive characteristic, metals share several other typical physical properties such as high thermal conductivity, high density, malleability and ductility. Several non-metallic elements exhibit one or more of these properties, so that the only feature that defines a metal unambiguously is the electric conductivity which decreases with increasing temperature. Within a given period the properties of the elements vary gradually from a high electropositive (metallic) character at the left-hand side of the series to the highly electronegative (non-metallic) character at the end of the series. The "metalloids" (or half metals) such as boron, silicon, germanium, arsenic and tellurium are balanced in the Periodic Table between metals and non-metals.

1.1 Trace elements

In earth's crust about 90 elements are found and 9 elements (*viz.*, Al, Fe, Ca, Mg, O, Si, Na, K and Ti) only account for over 99% by weight. The remaining 81 elements together account hardly 0.1% by weight are called as "trace elements" (Wittmann, 1979; Dara, 1997). Out of about 40 naturally occurring elements detected in living organisms, about 25 seem to be highly "essential" for the higher animals (Dara, 1997). These include Na, K, Ca, Mg, V, Cr, Mn, Fe, Co, Cu, Mo, Zn, Sn, H, C, N, O, Si, P, S, Se, F, Cl, Br and I. The essential elements have a normal distribution pattern in the animal body. These elements Al, Sb, Hg, Cd, Ge, V, Si, Rb, Ag, Au, Pb, Bi, Ti, etc. are believed to be acquired by the animal body as environmental contaminants due to contact of the organism with the environment. These elements are usually unevenly concentrated in different organs and are called as "non-essential elements".

1.2 *Heavy metals*

The term "heavy metal" is widely used in scientific literature with reference to several elements beginning with beryllium and going upto actinides (Nair, 1984). The heavy metals are generally regarded as having an atomic numbers of 22 to 92 in all groups from period 3 to 7 in the Periodic Table (Waldichuk, 1974). The Monitoring and Assessment Research Centre (MARC) at Chelsea College, London broadly defines the term "heavy metals" as metals of atomic weight higher than that of sodium and having a specific gravity of more than 5.0 (*i.e.*, densities above 5 g/cm^3). This definition includes over 70 metallic elements, although only a few of them are recognised as potentially damaging (Piotrowski and Coleman, 1980). The term "trace metal" may describe a metal found in trace amounts in an organism (*e.g.*, less than 0.01% of the mass of the organism (Wittmann, 1979) or may have a further restriction and apply only to those metals required in metabolism (Rainbow, 1988)

1.3 *Toxic metals*

Although at natural concentrations, trace elements either constitute the prosthetic group of enzymes or function as enzyme activators, at elevated concentration they act as inactivators of enzyme systems and as protein precipitants (Nair, 1984). Metals in their pure state present little hazard, except those having a high vapour pressure such as mercury and those which may be present in the particulate form in the atmosphere such as vanadium. It is the soluble compounds of the metals which create the problems in the aquatic environments. The different oxidation states of metals determine certain degree of toxicity in aquatic organisms. The power of the elements to attract and accept electrons in compound formation is called "electronegativity", which has definitely some bearing on its ecological effects, with respect to toxicity to aquatic orgnims. The electronegativity if more, the toxicity will also be more (Waldichuk, 1974; Wittmann, 1979). The metals are classified into (i) very toxic-effects seen at concentration below 1 ppm, (ii) moderately toxic-effects appear at concentrations between 1 and 100 ppm, and (iii) scarcely toxic-effects rarely appear (Nair, 1984). Examples of very toxic metals include the cations Ag^{+}, Be^{2+}, Cu^{2+}, Hg^{2+}, Sn^{2+}, Co^{2+}, Ni^{2+}, and Pb^{2+}. Moderately toxic metals include anions of As^{III}, As^{IV}, Mn^{VII}, Mo^{VI}, Se^{IV} and V^{V}, and the cations Al^{3+}, Ba^{2+}, Cd^{2+}, Cr^{3+}, Fe^{2+}, Mn^{2+} and Zn^{2+}. Some of the scarcely toxic elements include Rb^{+}, Sr^{2+}, Ti, etc.

The priority list of pollutants compiled by the Environmental Protection Agency of United States contains the eight more widespread heavy metals - arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc (Moore and Ramamoorthy, 1984). According to Dara (1997) Hg, Pb, Cu, Cd, Zn, Ni, etc. are generally known as "toxic heavy metals" and Cu, Co, Mn, Mo, Se and Zn as "essential heavy metals". According to George (1987) the toxic metals are aluminium, arsenic, antimony, cadmium, chromium, copper, iron, manganese, mercury, lead, uranium, zinc, etc.

Minute traces of As, Cr, Ni and Sn have been found to be essential for animals, but not for plants (Dara, 1997). Some essential physiological roles have been inferred for As, Cd and Pb. Hg and Ag have not yet been confirmed to be essential both for plants and animals since they do not seem to serve any useful biological function. Comparative toxicity of the eight most important heavy metals are listed below (Piotrowski and Coleman, 1980; Moore and Ramamoorthy, 1984). But, their toxicity varies from species to species and environment to environment.

Metal	Essential in Mammals	Toxicity to Humans	Toxicity to aquatic organisms		
			Plants	Invertebrates	Fish
Hg	–	High	High	Variable	High
Pb	–	High	Low-medium	Medium	Medium
As	–	Very-high	Variable	Variable	Very-high
Cu	+	Low-medium	High	High	High
Cd	–	Medium	Low-medium	High	Medium
Ni	+	Medium	Low-medium	Low	Low
Cr	+	Low	Low	Low	Low
Zn	+	Low	Variable	Low	Medium

1.4 Trace elements for plankton production

Phytoplankton is the primary producer of the aquatic ecosystem. To carryout photosynthesis and further growth it requires a number of inorganic nutrients/elements such as nitrogen, phosphorus, potassium, sulphur, calcium, magnesium, zinc, manganese, molybdenum, iron, copper, chlorine, boron, cobalt, iodine, silicon, sodium, vanadium, etc. (Padmavathi and Durgaprasad, 1995). If the water is deficient in any of these required nutrients, plankton will not develop at optimal levels resulting in the poor production of the dependent cultured organisms. The elements such as Zn, Mn, Fe and Cu are needed by all algae.

Zinc serves as an activator in some enzymatic reactions and plays an important role in photosynthesis. Another metabolic role of zinc is in the synthesis of protein. Manganese plays an important role in nitrogen metabolism and it is probably an essential requirement for algae. In Mn deficient waters, photosynthesis is lowered, since Mn is a very important activator of enzyme systems, especially those involved in the oxygen evolving part of photosynthesis, respiration, nitrogen metabilism and assimilation. Mn compounds are deposited on and in the cell walls of some algae *e.g.*, desmids such as *Penium* and *Closterium* and the thecae of *Trachelomonas*. Molybdenum is an essential element for nitrogen-fixing blue-green algae. Iron has long been known to be essential to algae. It is a key element in metabolism being a constituent of the cytochrome molecule. The rate of photosynthesis is lowered by iron deficiency. Iron is necessary in chlorophyll construction. Copper is essential, but at high concentrations, it is an algal poison. Boron deficiency produces a loss of pigment and reduction of growth in *Nostoc muscorum*. Cobalt is a constituent of vitamin B_{12}. Cobalt or cobalt combined organically in vitamin B_{12} (cobalamin) has been shown to be essential for large number of algae. Silicon is an absolute requirement for diatoms to build their frustules (cell wall) and for some species of Chrysophyceae and Xanthophyceae.

1.5 Effect of heavy metals on aquatic life

The impact of pollutants on marine environment is more acute and its deleterious effects on living resources are much more evident in coastal and estuarine areas than the open ocean. Besides being the most fertile part of the marine ecosystem and important feeding, nursing and passage zones for a large number of commercially exploitable aquatic species, coastal and estuarine regions are chief recipients of man-made and natural pollutants.

The effect of the pollutants containing heavy metals has been reported in different aquatic species by different authors. Bryan (1971) has shown the inhibition of growth of *Laminaria digitata* by zinc, lead and copper. In the case of zooplankton, Qasim *et al.* (1988) have noted the high concentration of all metals except mercury. Benthic macrofauna such as polychaete worms, crustaceans, bivalves and echinoderms occurring in the sediments rich in heavy metals showed varying degree of accumulation of the metals in their tissues, resulting in high contents even in habitats with low metal concentrations (Everaarts *et al.*, 1989).

Some heavy metals have high affinities for ligands containing sulphur and nitrogen, and hence are bound easily to organic molecules such as proteins (Nieboer nd Richardson, 1980). "They, therefore have the capacity to be incorporated into biological molecules to play roles in metabolism and thus to be selected in evolution as essential metals. Similarly, however such high affinities for biological molecules also provide heavy metals with the potential to play toxic roles, for example by substituting for an essential metal of lower affinity in a biologically active molecule or by binding elsewhere onto such a molecule, in either case distorting the geometry of the molecule and thereby inhibiting its function. Thus, all the heavy metals have the potential to be toxic whether essential or not" (Rainbow, 1988).

The salts of cadmium, copper, mercury, lead, zinc, iron and trivalent chromium are more toxic to fish than the elementary forms (Metelev *et al.*, 1983). The harmful effect of salts of heavy metals is by the following ways : (a) action of precipitated insoluble hydroxides of metals deposited on the gills and eggs cause mortality of both eggs and fish, (b) some compounds of heavy metals reduce the pH of the water on hydrolysis, and (c) specific toxic effect (Metelev *et al.*, 1983). Respiration of fish is disturbed as a result of the direct action of salts of heavy metals on the respiratory epithelium of gills. A thich membrane of coagulated mucus on skin and gills of fish, forms after poisoning with all heavy metals affecting gaseous exchange between the medium and the gill lamellae. The white coating of the mucus layer is the result of chemical reaction between metal ions and the mucus secretion.

1.6 Bioaccumulation

In contrast to the non-essential trace metals such as lead, cadmium, mercury, arsenic, the essential metals such as copper, zinc, iron and cobalt have important biochemical functions in the organisms. They form either an electron donor system or function as ligands in complex enzymatic compounds. Since essential elements are only used by the organisms in trace amounts and generally as they exist in the environment in small concentration, their enrichment in the organisms does not exceed the level which allows the enzyme system to function without interference. This means that the concentrations of essential trace elements are generally higher in the organisms than in water. If there is excess in the body, the metal content in the organism can be regulated by homeostasis (Bryan and Hummerstone, 1973). However, if the heavy metal concentration at the source of supply (*e.g.*, water, food) is too high, the homeostatic mechanism ceases to function and the essential heavy metals act in either acutely or chronically toxic manner. Thus, in the event of a resulting extended bioaccumulation of heavy metals, the organism may be damaged.

The accumulation of metal in fish, is a function of uptake and excretion. Uptake is considered to be passive and involves diffusion gradients created by adsorption or binding of the metal to the tissue and cell surfaces (Bryan, 1976). The gills of teleosts are likely sites of metal uptake from the ambient water due to their large surface area and the close proximity of the internal constituent of the body and external environment. Within the body, the degree of accumulation in various tissues is dependent on the binding of the metal to specific ligands. Liver and kidney are the organs with specific metal binding proteins, and these are organs which are the targets of the toxicant action and accumulate metals to significant levels (Stagg and Shuttleworth, 1982). Dallinger *et al.* (1987) stated that as far as fish is concerned, there are three possible ways by which metals may enter the body: (i) the body surface, (ii) the gills, and (iii) the alimentary tract. But little is known about the uptake of heavy metals through the skin. It can be assumed that the body surface of fish is more or less impervious to harmful substances in the surrounding water (Dallinger *et al.*, 1987). There are some indications that mucus secretion may prevent heavy metals from entering the bdy of fish (Eddy and Fraser, 1982). So it may be assumed that the gills and gut are both important pathways for metal uptake in fish (Wills and Sunda, 1984). The work of Honda *et al.* (1983) on heavy metals in organs and tissues showed high concentration of metals in liver and low levels in muscle. However, relatively high concentration of manganese, sinc, copper, lead and nickel was recorded in ovary and testis, and manganese and zinc in the skin. The concentration of metals in the organs and tissues characteristically changed with the growth of the fish. The small fish show faster uptake and excretion rates of metals than the larger ones.

Mechanism of heavy metal detoxification in invertebrates is well documented (Noel-Lambot, 1976; Viarengo *et al.*, 1980). Heavy metals are bound to metal binding proteins or stored in cellular structures such as in vacuoles and lysosomes (Bouquegneau *et al.*, 1984). Zinc is excreted into the digestive tract and about 45% of it is eliminated with the faeces (Baudin, 1981). Noel - Lambot (1981) found white mucus corpuscules in the intestinal lumen of fishes. In fish intoxicated with $CdCl_2$, $ZnCl_2$ or $CuCl_2$ added to sea water, mucus corpuscules in the intestine contain enormous concentrations of these metals. It seems therefore, they limit the entry of the metals through the intestinal wall. The heavy metals are eliminated predominantly by the kidney or by the bile (Grahl *et al.*, 1985).

The effect of heavy metals on different aquatic organisms is often complex and difficult to interpret. Dissolved oxygen, pH, salinity, temperature and hardness of the water have been demonstrated to be factors that influence the physiology of an organism and the rate of uptake of heavy metals (Wittmann, 1979; Waiwood and Beamish, 1978; Winner, 1985; Bradley and Sprague, 1985 a; Everall, 1987; Chaudhari *et al.*, 1996). In general, salinity in the marine environment is relatively constant and has little influence on the heavy metal concentration compared to their role in estuaries. In estuaries, salinity however, plays a dominant role in influencing the metal concentrations in free water and organisms (Wittmann, 1979). In sea water, the dissolved heavy metal concentrations are generally much lower than in freshwater.

Moreover, the high salt contents alter the pH of the milleu and consequently the metal solubility. In the case of brackishwater organisms the negative potential difference of the inner body wall increases with lower salinity (Fletcher, 1970); ion transport into the organisms consequently increases. Bryan and Hummerstone (1973) demonstrated through laboratory experiments on *Nereis diversicolor* that the absorption rate of zinc per mass unit and time period increases with rising salinity. In case of copper no direct correlation could be established and seen apparently plays only a secondary role.

The major factors involved in determining the seasonal fluctuatioin of trace metal levels in aquatic biota are the extent of pollutant delivery into the aquatic environment, the weight changes occurring in the organisms and the direct effects of salinity, temperature and other water qualities which vary seasonally (Phillips, 1980). It is clear that an increased ambient supply of metal will lead to more rapid uptake of that metal by organisms. Several physiological changes occur in organisms with seasons and may cause fluctuations in the trace metal levels present either in the whole organisms or its component tissues (Philips, 1980).

Sediment/detritus feeders particularly benthos are exposed to metals both in solution and through ingestion of metal-enriched particulate material (Louma, 1983). Concentration of trace metals in the pelagic species such as sardine, mackerel and squid was found to be lower than that of benthic animals such as carb and prawn (Krishnakumar *et al.*, 1990). Difference in heavy metals concentration in various species is attributed to varying feeding habits (Nair *et al.*, 1997). It has been shown for instance, that bottom dwelling fishes accumulate heavy metals, because of their association with metal containing sediments (Ney and Van Hassel, 1983). And also bottom water in estuaries contains more amount of heavy metals than the surface waters (Mohapatra, 1993).

The capability of some marine animals and plants to accumulate potentially toxic trace metals in their tissues, far in excess of ambient level is well known and has become the focus of increasing number of studies form the Indian waters (Zingade *et al.*, 1976; Sankaranarayanan *et al.*, 1978; Agadi *et al.*, 1978; Kureishy *et al.*, 1981, 1983; Lakshmanan and Nambisan, 1983; Patel *et al.*, 1985; Pillai *et al.*, 1986; Mohapatra, 1993; Krishnakumar *et al.*, 1998). The bivalve molluscs accumulate pollutants in their tissues and species of the genera *Mytilus* and *Crassostrea* have been used with considerable success in various monitoring programmes (Goldberg *et al.*, 1978; Martin, 1985; Phillips, 1985).

1.7 Monitoring

Biological monitoring is a means of assessing water quality or the toxicity of chemicals employing living organisms as the sensors. Relatively recent environmental regulations have lead to the application of biomonitoring techniques to waste water discharges and chemical industries. Classical approaches to biomonitoring have included acute bioassay which takes death as the end-point of the test. Recent developments include automated and real time biomonitors which utilise computer technologies for assessing changes in physiological or behavioural parameters to indicate the presence of toxics (Sivasankaran, 1990). In biomonitoring models the changes measured in the biological response of the test animals used, are likely to reflect a meaningful change in the chemical and/or physical conditions of the water concerned. Toxicological hazards measured by bioassay procedures may therefore, be more realistic than those predicted from the results of chemical analyses and the available information on the toxicity of the compounds detected (Koeman *et al.*, 1978; Genjatulin, 1990). Since 1950s, the acute toxicity testing has become the "workhorse" in monitoring pollution effects (Buikema *et al.*, 1982). Information generated from various toxicity tests can be of use in the management of pollution for the purpose of (a) prediction of environmental effects of a waste,

(b) comparison of toxicants on animals or test conditions and (c) regulation of discharge.

Various groups of aquatic organisms including bacteria, algae, molluscs and fish may serve as indicators for continuous biomonitoring of the media or environment. Lesions in organs such as gills, liver and kidney of fish may be indicative for the presence of certain toxic agents (Koeman *et al.*, 1978). Early sign of spinal and vertebral aberations are the indications of compounds such as Zn^{++} and Cd^{++} (Bengtsson, 1975). The lower "RNA - DNA" ratio and "ALP - ACP" ratio in the muscle tissue and blood serum of fish respectively may predict the pollution interface in fish health and growth (Mohapatra and Noble, 1992; Mohapatra and Shanmugam, 1995). Haematological analysis was done by Banerjee and Homechaudhuri (1990) to assess copper toxicity in a bio-indicator fish *Heteropneustes fosslis*. Results showed that the copper content in the blood plasma increases simultaneously with the lethally toxic copper ion in the waterbody. It is apparent that a slight increase in the plasma copper content sufficiently indicates copper toxicity in fish. The blood respiratory characteristics are also significantly altered in copper toxicity. Being easy and accurate to measure, both alteration in the blood characteristics and the plasma level copper seem to be useful as reliable tools for bio-indication of aquatic copper pollution hazards to nektonic life.

The glycogen - protein and glycogen - lipid ratios decrease with increasing exposure of *Mytilopsis salliei* to cadmium (Devi, 1996 a). The bivalves prefer to depend on carbohydrates and proteins rather than on lipids for their utilisation on exposure to either sublethal or lethal stress of Cd. The decrease in oxygen consumption together with the utilisation of glycogen and carbohydrates during Cd exposure suggests that the bivalves might shift to anaerobic metabolism in order to encounter the heavy metal stress in the environment. In metal toxicity the oxygen consumption in bivalves decrease (Devi, 1996 b).

Various biochemical techniques are used for biological effects monitoring, both in general assessment monitoring and in studying the health of degraded habitats or "hot spots". There are several techniques which might have not been tested in the field, but may be of use in future monitoring studies. These include RNA/DNA changes, mutagenicity/carcinogenicity testing, stress hormones, variations in carbohydrate or lipid metabolism as well as membrane, immunological and neurological responses.

Aquatic toxicology has been defined as the qualitative and quantitative study of adverse or toxic effects of chemicals and other anthropogenic meterials on aquatic organisms. The subject also includes the study of transport, distribution, transformation and ultimate fate of chemicals in the aquatic environment. In this field of science, studies of the biochemistry and function of biotransformation enzymes in aquatic organisms hold a central role. Metabolism or biotransformation through the phase I (cytochrome P-450 monooxygenase enzymes) and phase II (conjugating enzymes) pathway is a requisite for detoxification and excretion of lipophilic chemicals. In addition, such a transformation is also responsible for the activation of foreign chemicals to the intermediates that ultimately result in toxicity, carcinogenicity, and other adverse effects. The dual role of many of these enzyme systems, being involved in both xenobiotic and endogenous metabolism, furthermore makes interactions between foreign chemicals and physiological processes possible. Lastly the response of some of these enzyme systems, in particular the cytochrome P-450 1A1 subfamily, to organic xenobiotics makes analysis of enzyme levels by catalytic or immunochemical methods a potent way to monitor pollutioin effects at the molecular level.

Polyclonal antibodies (PAb anti-perch P450 1A) raised against the cytochrome P450 1A orthologue in perch were used to quantify hepatic P450 1A in fishes used or proposed to be used in Swedish environmental biomonitoring programmes. Protein blots revealed that the PAb anti-perch P450 1A recognised one major β-napthoflavone-inducible microsomal protein band in all studied fish species (feral perch, pike, dab and blenny, and the hatchery reared rainbow trout and lake trout). All feral fish exhibited elated P450 1A levels, with the highest levels found close to industrial or municipal discharges. This indicates that immunochemical assays can be used to detect the induction of P450 1A in environmental biomonitoring (Forlin and Celander, 1993).

The widespread distribution of metallothioneins (MTs) in aquatic animals is firmly established, having been reported for atleast 80 species of fish and invertebrates (Roesijadi, 1992). Special biological functions are attributed to various forms of MTs. The notion that metal-binding by MT is protective of cellular function. In a number of cases, MT induction or increased levels of MT-bound metals in individuals in metal-contaminated environments can be used to justify continued development and testing of diagnostic markers of metal exposure based on MT function.

The bivalve molluscs accumulate pollutants in their tissues and species of *Mytilus* and *Crassostrea* have been used with considerable success in various monitoring programmes (Goldberg *et al.*, 1978; Martin, 1985; Krishnakumar *et al.*, 1990). The green mussel *Perna viridis* has been proposed as a biomonitor of heavy metals in tropical waters (Phillips, 1985). *Crassostrea cuculata* can be used as a suitable bio-indicator of mercury contamination in the coastal environment (Krishnakumar and Pillai, 1990).

In the long run, the sub-lethal concentration may prove more deleterious than the lethal concentrations, because subtle effects on the fish may alter their behaviour, feeding habits, positioin in the school, reproductive success, etc. Subtle effects at the organ or cellular level may alter the metabolism of the fish, and hence its ability to withstand the stress. Even if the fish and other aquatic organisms are not directly affected by the pollutants, they are liable for infection or toxication if they consume food which was contaminated by pollutants.

To evaluate the level of pollution, the "baseline" or background has to be established for several heavy metals in various near-shore and estuarine environments. They can be used as references for monitoring possible future metal pollution.

The water quality standards are (i) to first determine the pollutant concentration whether it is acutely toxic to the organism or not, and (ii) to estimate the pollutant concentration that will have no adverse effect on the organism by multiplying the acutely toxic concentration by a so called "Application Factor". Typically the application factor is a number on the order of 0.01 - 0.1 (Laws, 1981).

It is very clear that there is a global awareness in recent years on pollution and its adverse effects both in the terrestrial and aquatic environments, which meet the food requirements by way of agriculture, fishing and aquaculture for the ever increasing human population. This calls for an urgent monitoring of nature, source and the amount of pollulants entering into the environment; factors contributing to the pollution, toxicity of the pollutants to organisms, its effect on food resources, remedial measures and legislation.

2

TOXICITY OF METALS AND DISEASES CAUSED BY THEM

The United States Environmental Protection Agency (USEPA) has divided metals into two categories *viz.* hazardous and non-hazardous. The hazardous group *(e.g.* mercury and beryllium) is the most dangerous as it can endanger human health even on a slight exposure. Hazardous candidate metals are potential hazards indicating that they must be kept under surveillance and review *(e.g.* Cadmium, lead, barium, copper, nickel, tin, etc.). Antimony and arsenic though known to be toxic to human beings, are not included in these lists, because their concentrations in the environment are very low (Sharma, 1995). In general, a toxic metal may be defined as one which is neither essential nor beneficial, but exhibits a positive catastrophic effect on normal metabolic function even when present in small amounts.

The toxicity of a metal depends on its inherent capacity to adversely affect any biological activity. Toxic metals change the biological structures and systems into inflexible and irreversible conformations leading to deformity in the body or finally death (Kudesia, 1980). Almost all metals are toxic at higher concentrations and some are lethal even at very low concentrations.

Some of the trace metals play essential roles in biological processes, but at higher concentration they may be toxic to biota. For microalgae and natural population of phytoplankton copper is the most toxic and lead is the least toxic heavy metal. The heavy metals have a great affinity for sulphur and attack the -SH bonds in enzymes, thereby immobilizing the latter. Protein carboxylic acid groups (-COOH) and amino groups ($-NH_2$) may also be attacked by the heavy metal ions.

Although the toxic action of different metals may be different, most of them involve binding to the metabolically active groups such as amino-, sulphydryl-, carboxyl-, phenolic- or phosphoryl- groups. The toxicity of a metal is mainly determined by its solubility, stability and biological reactivity. Chromium, nickel, cadmium and beryllium have been found to be potentially carcinogenic, beryllium, chromium radionuclides such as ^{90}Sr and ^{239}Pu have been found to be potentially mutagenic. Cd, Cu, Pb, Hg, Mo, Ni and Se in excessive amounts have been found to be potentially teratogenic. Some arsenic compounds are carcinogenic, mutagenic as well as teratogenic (Dara, 1997).

All forms of mercury are toxic. But the intensity of toxicity varies considerably. Inorganic mercurials are considered as the least toxic. Of the inorganic forms, the mercury vapour is the most hazardous as it can diffuse through lungs into the blood and then into the brain. Inorganic mercuric compounds are very slowly absorbed from the gastrointestinal tract, however even when absorbed, they get eliminated quite rapidly in the urine. Organic mercurials are divided into alkyl mercurials and aryl mercurials. Aryl mercurials once absorbed gets broken down to the relatively less toxic inorganic derivatives in the tissues, which gets eliminated through urine. Aryl mercurials are most toxic, because they are stable and have fairly long retention time in tissues, thus tending to accumulate to high concentrations. The harmful effects of alkyl mercurials is due to their lipid solubility which gives them an affinity for nerve tissues. Mercury poisoning results in chromosomal damages resulting from the combination of mercurials with SH groups of enzymes and amino acids.

In the aquatic environment, the less toxic metallic mercury is converted to the highly toxic methyl and dimethyl derivatives by the anaerobic microbe *Clostridium cochlearium*. Many strains of *Pseudomonas* sp. effect the same transformation aerobically. Under anaerobic conditions mercuric ions may combine with hydrogen sulphide to form mercuric sulphide. The poorly soluble mercuric sulphide gets converted to soluble mercuric sulphate with aeration which may then be methylated biologically.

Shellfish found in contaminated water are capable of bioaccumulating and concentrating lead to an alarming level. In human being the absorption of lead is slow and the excretion is ever slower (Sharma, 1995). Thus the metal tends to accumulate. Most of the lead is taken up by red blood cells and is circulated through the body where it initially gets concentrated in the liver and kidneys. Thereafter, it is redistributed to bones, teeth and brain. The immobilised lead in the bone is a potential hazard. Lead interferes with the synthesis of haemoglobin.

Most of the trace metals are cumulative poisons which are not detoxified by metabolic activities and most of the living organisms bioaccumulate them.

Serious damages at cellular level of hepatopancreas of *Perna viridis* exposed to various concentrations of copper and mercury are reported by Pillai and Menon (1998). George *et al.* (1995) reported the swelling (hypertrophy) of the renal tubular linning epithelial cells in *liza parsia* exposed to 0.05 and 0.1 ppm mercuric chloride for 15 days. The results of histopathological studies that the concentration as low as 100 and 300 ppb of Zn bring about destructive and deteriorative changes in the hepatopancreas and gills of *Penaeus indicus* (Viswanathan and Manisseri, 1995)

2.1 *Toxicity to human beings*

In 1953, 52 persons living in fishing villages along Minimata Bay, Japan died of a mysterious disease. Investigations revealed that the victims had eaten shellfish contaminated with mercury containing effluent from a nearby plastic industry, Shin-Nihon

Chisso Hiryo Co. The methyl mercury compounds present in the effluent wastes discharged into the Minimata Bay were gradually bioconcentrated by fish and shellfish in the bay. The ailment became known as "Minimata disease" characterised by peculiar neurological disorders. The other instance of mercury poisoning came to be known in the year 1972 when 450 Iraqui villagers died after consuming grain which was treated with mercury containing pesticides.

Cadmium is highly toxic, because of the absence of homeostatic control for the metal in the human body. It is stored in the kidney, causes hypertension, respiratory disorders, aminoaciduria, hypercalciurea, glucosuria, proteinsuria, osteoporosis, formation of kidney stones, etc. The disease specifically associated with cadmium poisoning was recognised in Japan. People residing along the banks of Junstsu River in North Japan were consuming the rice which was contaminated with cadmium and they were ingesting 100 to 1000 µg of cadmium every day. At the end of 1965, about 100 deaths were reported. The victims accumulated about 500 to 600 mg of cdmium in their body over several years. The illness is called as "Itai-Itai" (or Ouch-Ouch) disease. The disease was characterised by kidney malfunction, drop in the phosphate level of the blood serum, loss of minerals from the bones and osteomalacea (bone fracture and intense pain). Concentrations of cadmium in the rice grown in polluted areas were found to range between 0.6 and 1.0 µg/g.

Lead is considered as a general protoplasmic poison which is cumulative, slow-acting and subtle. Lead inhibits several important enzymes involved in the overall process of heme synthesis, obstructs the utilisation of oxygen and glucose for life sustanining energy production. When blood lead level reaches about 0.8 ppm, symptoms of anaemia will be observed due to the deficiency of haemoglobin. Higher level of lead in the blood can cause kidney dysfunction and brain damage, because of its toxic nature to central and peripheral nervous system. One of the insidious effects of inorganic lead is its ability to replace calcium in bones and accumulate there as a reservoir for long-term release. Organic lead, as tetra-ethyl lead and tetra-methyl lead is more acutely poisonous (10 to 100 times) than inorganic lead (Dara, 1997). Inorganic lead can bind to complexing agents such as calcium - EDTA or to thiol groups, but organic lead does not. Organic lead compounds such as tetra-ethyl lead can penetrate the skin and absorb into the body tissues more repidly as compared to inorganic lead compounds.

[Trivalent chromium (Cr^{+3}) is found to be essential to human and animals. Hexavalent chromium (Cr^{+6}) is better absorbed than Cr^{+3}].

Arsenic is a protoplasmic poison. Trivalent arsenicals react with sulphydryl (-SH) groups in cells and thus, inhibit the sulphydryl containing enzyme systems essential to cellular metabolism. Soluble arsenicals are absorbed from cell mucous membrance. The "black foot disease" is caused by the chronic ingestion of inorganic arsenic. Arsenic is toxic to liver and causes necrosis and cirrhosis. Arsenic poisoning affects the bone marrow and cellular elements of blood.

Selenium is more toxic than arsenic. Chronic selenium poisoning was reported in 1925 in copper refinery workers and the symptoms observed were sore throat, coryza and gastrointestinal irritation. Dermatitis, red staining of fingers, teetch and hair were also reported. It is mutagenic and teratogenic. Selenium toxicity occurs mainly in neutral and alkaline areas in which the soluble selenates are formed. In acidic condition selenite ion (SeO_3^{2-}) formatiion is favoured which forms insoluble complexes with ferric ions, thus rendering the selenium unavailable.

The toxic effects of some of the metals to human beings are summarised below (Sittig, 1973; Kudesia, 1980; Dara, 1997; Mathew, 1991 a & b):

Elements	Effects
As	Skin cancer, dermatitis, bronchitis.
(725 mg As in body)	Vomiting, diarrhoea, nausia, irritation of nose and throat, abdominal pain, skin erruptions, inflamations.
Au	Fever, violent diarrhoea, gastritis, colitis.
Ba	Benign pneumoconiosis known as baritosis, effect on veins.
(>100 mg Ba in body)	Excessive salivation, colic, vomiting, diarrhoea, tremors, Muscular paralysis of nervous system.
Be	Peumonitis, beryllìosis (affecting heart), cancer, non-healing of ulcer, bone tumours, inflamation of pulmonary tissue.
Cd	Toxic to all systems and functions of the body, bronchitis, kidney damage, carcinogenic, affects heart and liver.
(50 mg Cd in body)	Vomiting, diarrhoea, abdominal pains, loss of consciousness, growth retardation, bone deformation, hypertension, impaired reproductive function, tumor formation, teratogenic effects.
Co	Intracellular hypoxia, polycythemia, goitre.
(27 mg Co in body)	Paralysis, low BP, lung irritation, bone defects, diarrhoea.
Cr	Irritation of the skin and respiratory tract, dermatitis, ulcers, cancer of respiratory tract, growth depression.
(>70 mg Cr in body)	Cancer, anuria, nephritis, gastrointestinal ulceration, nervous disorder.
Cu	Excessive salivation, epigastic pain, nausia, vomiting, diarrhoea.
(470 mg Cu in body)	Hypertension, sporadic fever, uremia, coma.
Fe	Necrotising gastroenteritis, tissue damage.
(10 mg Fe in body)	Rapid increase of respiration, pulse rates congestion of blood vessels, hypotension, drowsiness.
Hg	Loss of vision, hearing and intellectual abilities, nervous disorder.
Mn	Loss of memory, impotence, eye diseases, manganese psychosis (brain disease), pneumonia.

Elements	Effects
(>100 ppm Mn in body)	Growth retardation, fever, sexual impotence, muscle fatigue, blindness.
Mo	Molybdenosis : defects in osteogenesis, skeletal and joint deformity, spontaneous subepiphysial fracture and mandibular exostoses.
Ni	Cancer in lungs and sinus, dermatitis, disorder in respiratory system.
(>30 mg Ni in body)	Changes in muscle, brain, lung, liver and kidney leading to cancer, tremor, paralysis.
Pb	Anaemia, cardiac disease, kidney damage, reduce antibody synthesis optical atrophy, tremors, wrist drop, encephalopathy.
(>800 mg Pb in body)	Brain damage, loss of apetite, vomiting, convulsions, uncoordinated body movements, mildanemia, coma, death.
Sb	Similar poisoning effect as arsenic.
Se	Lacrimation, palpebral oedema, conjunctivities, sneesing, anosmia, coughing, loss of hair, changes in fingernail morpholgy, skin lesions, paralysis, dental caries.
(>4 mg Se in body)	Fever, nervousness, vomiting, fall of BP, liver, kidney and spleen damage, blindness.
Sr	Respiratory failure, raising of BP.
V	Fertility loss, cancer.
Zn	Fever, pneumonitis, dermatitis, lethargy, interference with the metabolism of other trace elements especially copper.
(>165 mg Zn in body)"	Vomiting, renal damage, cramps, pneumonitis.

2.2 *Toxicity to aquatic animals*

Poisons especially salts of heavy metals exert a depressive action on fish. Most of the salts of heavy metals produce toxic effect on fish through physical accumulation. Orange-yellow liquid is visible in the abdominal cavity of the fish in hexavalent chromium toxicity. The toxicity of Cr to aquatic life is less as compared to Cd, Hg and Pb. Chromium at 10 ppm levels in water is considered to be toxic to several species of algae. Lead and selenium destroy the erythrocytes and change the blood serum to red. In the case of Cu, Hg and Ag the toxic effect is observed even at concentration 0.02 to 0.004 mg/l (Metelev *et al.*, 1983). In nickel poisoning the gills of the fish are covered with mucus and turn dark in colour. In trivalent iron toxicity brown coating is formed on the gills. Arsenic is slow acting posion for fish and other aquatic organisms. Arsenites penetrate the fish body more rapidly than arsenates and are more toxic. The toxicity of arsenic to aquatic biota generally decreases with increasing pH of the medium. The toxicity of lead is slightly less than that of Hg, Cu and Cd. At a concentration 0.1 to 0.4 mg/l the symptoms of poisoning are discernible. Gills and skin are covered with mucous. Lead acts locally on bronchial apparatus. Lead acts haemolytically and arsenic paralytically. Zinc compounds damage the gills of fish very severely and cause enhancement of mucous discharge. A concentration of 15 mg/l is toxic for all fish within 8 hours (Metelev *et al.*, 1983). Zinc is less toxic to fishes as compared to Hg, Cd, As and Cr. Copper in excessive amount may cause hemolysis, hepatotoxic and nephrotoxic effects. Mercury and its compounds ($HgCl_2$, $HgSO_4$, $HgNO_3$) are highly toxic for fish and other aquatic organisms. In soft water a concentration of 0.01 mg/l is lethal for fish (Metelev *et al.*, 1983). Gills of the fish are destroyed. In silver poisoned fish, the gills acquire a musty brown colour and are very severely damaged. Cadmium in water at 10 ppm level can kill fishes in one day while at 1 ppm level they will be killed in 10 days (Dara, 1997). Hardness and salinity of water provides some degree of protection. Amongst the aquatic invertebrates the crustceans are more sensitive to cadmium toxicity as compared to molluscs and polychaetes. Nitrates of Cu, Zn, Cd and Ni are more toxic than their sulphates. Chlorides and nitrates of copper are toxic even at a concentration of 0.01 to 0.02 mg/l. Bluish mucous coating are seen over the gills. Silver nitrate is very toxic for fish and algae.

There are some reports available on the toxicity of the heavy metals on fishes and other aquatic animals through bioassaying. Some of them are reviewed and presented below :

Species	Element	LC50 (ppm)	Source
Oncorhynchus mykiss	As	144hr LC50 = 18.5	Rankin and Dixon, 1994
Lebistes reticulatus	$CdCl_2$	96hr LC50 = 250.0	Sehgal and Pandey, 1984
Moina mongolica	Cd^{2+}	48hr LC50 = 3.89	Yuxin and Zhihui, 1991
Red Sea bream (*Chrysophrys major*)	Cd	96hr LC50 = 0.27	Weiguang and Chen, 1991
Mytilopsis sallei	Cd	96hr LC50 = 0.71	Devi, 1996 a
Emerita sp.	Cd	96hr LC50 = 1.35	Mohan *et al.*, 1984
Donax spiculum	Cd	96hr LC50 = 1.8	"
Perna viridis	Cd	96hr LC50 = 2.5	"
Sabellaria clandestinus	Cd	96hr LC50 = 2.8	"
Modiolus carvalhoi	Cd	96hr LC50 = 5.6	"
Moina mongolica	Cr^6	48hr LC50 = 4.24	Yuxin and Zhihui, 1991
"	Cu^{2+}	48hr LC50 = 0.09	"
Anadara granosa	Cu	96hr LC50 = 0.06	Kumaraguru and Ramamoorthy, 1978
Meretrix casta	Cu	96hr LC50 = 0.072	"
Crassostrea madrasensis	Cu	96hr LC50 = 0.088	"
Etroplus maculatus	$CuSO_4$	96hr LC50 = 1.83	Gaikward, 1989
Red Sea bream larvae	Cu	96hr LC50 = 0.07	Weiguang and Chen, 1991
Macrobrachium rosenbergii (PL)	Cu	96hr LC50 = 0.32	Ismail *et al.*, 1990
Perna indica	CuSO4	96hr LC50 = 0.08	Prabhudeva and Menon, 1998
"	Cu in nitrate form	96hr LC50 = 0.04	"
Liza parsia	Cu	96hr LC50 = 21.8	Mohapatra, 1993
"	$CuSO_45H_2O$	96hr LC50 = 85.6	"
"	Cu : Zn : Pb :: 23 : 20 : 57	96hr LC50 = 39.5	"
"	$CuSO_45H_2O$: $ZnSO_47H_2O$: $Pb(NO_3)_2$ :: 1 : 1 : 1	96hr LC50 = 106.7	"

Species	Element	LC50 (ppm)	Source
Tilapia nilotica	Cu	24hr LC50 = 73.4	Somsiri, 1982
	Cu	48hr LC50 = 63.9	"
"	Cu	72hr LC50 = 58.3	"
Pleuronectes flesus	Cu	48hr LC50 = 1.0-3.3	Jackim *et al.*, 1970
Fundulus heteroclitus	Cu	48hr LC50 = 3.2	"
Agosia chrysogaster (Longfin dace)	Cu	96hr LC50 = 0.86	Lewis, 1978
Ptychocheilus oregonesis (Northern squawfish)	Cu	96hr LC50 = 18.0	Andros and Garton, 1980
Tilapia nilotica	Hg	24hr LC50 = 3.98	Somsiri *et al.*, 1982
"	Hg	48hr LC50 = 3.8	"
"	Hg	72hr LC50 = 3.71	"
Moina mongolica	Hg^{2+}	48hr LC50 = 0.0034	Yuxin and Zhihui, 1991
Etroplus maculatus	$HgCl_2$	96hr LC50 = 0.67	Gaikward, 1989
Red Sea bream larvae	Hg	96hr LC50 = 0.004	Weiguang and Chen, 1991
Cirrhina mrigala fry	Hg	48hr LC50 = 0.16	Mohan *et al.*, 1986
Anabas tesudineus	$HgCl_2$	24hr LC50 = 1.5	Sinha and Kumar, 1992
Mytilopsis sallei	Hg	96hr LC50 = 0.2571	Devi, 1996 b
Penaeus monodon	Hg	LC50 = 4.0	Veena and Ammal, 1983
Oreochromis niloticus	NiCl	96hr LC50 = 27.2	Alkahem, 1994
Liza parsia	Pb	96hr LC50 = 64.7	Mohapatra, 1993
"	$Pb(NO_3)_2$	96hr LC50 = 103.5	"
Fundulus heteroclitus	Pb	48hr LC50 = 188	Jackim *et al.*, 1970
Oncorhynchus kisutch (Coho salmon)	Pb	48hr LC50 = 0.34	"
Goldfish	Pb	48hr LC50 = 117	Laws, 1981
Liza parsia	Zn	96hr LC50 = 13.7	Mohapatra, 1993
"	$ZnSO_4 7H_2O$	96hr LC50 = 60.3	"
Salmo gairdneri	Zn	incipient LC50 = 3.07-6.69 (4.53)	Bradly and Sprague, 1985 b
"	Zn	48hr LC50 = 3.3	Portman, 1972
Longfin dace	Zn	96hr LC50 = 0.79	Lewis, 1978
Northern squawfish	Zn	96hr LC50 = 3.69	Andros and Garton, 1980

Species	Element	LC50 (ppm)	Source
Nemacheilus botia	Zn	96hr LC50 = 25.0	Pundir, 1989
Salmo gairdneri	Zn	72hr LC50 = 2.0	Lovegrove and Eddy, 1982
Tilapia nilotica	Zn	24hr LC50 = 88.3	Somsiri, 1982
"	Zn	48hr LC50 = 74.8	"
"	Zn	78hr LC50 = 65.6	"
Red Sea bream larvae	Zn	96hr LC50 = 0.44	Weiguang and Chen, 1991
Channa punctatus	Zn	96hr LC50 = 23.07	Sen *et al.*, 1991
Penaeus indicus	Zn	96hr LC50 = 1.67	Viswanathan and Manisseri 1995

Based on the results copper was found more toxic than zinc and lead (Waldichuk, 1974; Mohapatra, 1993). The role of oxygen, pH, salinity, temperature and hardness in the environment have been demonstrated to be factors that influence the physiological state of an organism and the rate of uptake of heavy metals (Bryan, 1971; Waiwood and Beamish, 1978). Increased temperature and percentage of oxygen saturation of water increases the heavy metal toxicity, probably due to increased respiratory activity. It is known (collected from Metelev *et al.*, 1983) that the reduction in temperature by 10°C, the time of manifestation of poisoning symptom is accelerated by 1.9 to 3.4 times. Oxygen deficiency reduces resistance of fish to many poisons of organic and inorganic nature. The change in pH of the medium also influences the toxicity of metals on aquatic organisms. The toxic effect of heavy metals decreases in hard and sea water. Highly mineralised water containing Ca, K, Na, Mg and Ba salts decreases the solubility of toxic substances, forming insoluble sediments with them, and hence reducing their toxicity many times over. The organic compounds sometimes act as chelating agents for heavy metals and reduce their toxicity especially of copper and zinc. The salinity plays dominat role in metal toxicity. Adsorption rate of zinc per unit mass and time has been shown to decrease with increasing salinity (Chaudhari *et al.*, 1996).

2.3 *Additive or Synergistic effects*

Investigations made by Lloyd (1962) in England and Sprague and Ramsay (1965) in Canada have proved that the toxicities of pairs of poisons are additive. The Water Pollution Research Laboratory at Stevenage has gone further and proposed that toxicities in excess of two are also additive. In general when $A_s/A_T+B_s/B_T+C_s/C_T+....+N_s/N_T=1$, the water will be potentially poisonous to fish. In this expression A_s, B_s, C_s, etc. are the actual concentrations of the poison (metal in present context) present in the water and A_T, B_T, C_T, etc. are the corresponding threshold values.

Example (Mohapatra, 1993)

The 96 hr LC50 of 1:1:1 combination of copper sulphate, zinc sulphate and lead nitrate = 106.7 ppm on *Liza parsia,* a brackishwater fish. The individual contribution = (106.7)/3 ppm = 35.57 ppm.

The 96hr LC50 of copper sulphate	=	85.6 ppm
The 96hr LC50 of zinc sulphate	=	60.3 ppm
The 96hr LC50 of lead nitrate	=	103.5 ppm

$$\text{The toxic unit} = \frac{\text{actual concentration in solution}}{\text{lethal threshold concentration (LC50)}}$$

The toxic unit of copper sulphate	=	0.4155
The toxic unit of zinc sulphate	=	0.5898
The toxic unit of lead nitrate	=	0.3436

The toxic units are 0.4155 + 0.3436 = 1.3489 and is found greater than unit (*i.e.,* 1.0). Thus, the chemicals are indeed strictly "additive".

Combination of copper and zinc; copper, zinc and lead (Mohapatra, 1993); copper and cadmium; nickel and zinc are synergistic.

3

SOURCES OF METALS AND THEIR CONCENTRATIONS IN WATER

In 1965, Goldberg indentified the metals as normally occurring in sea water. The concentrations of metals in sea water are very low and the possibilities of contamination are high. Some of them are listed below :

Elements	Classification	Concentration (mg/l)
Al	T, C	0.01
V	T, C, H	0.002
Cr	E, C, H	0.005
Mn	T, C, H	0.002
Fe	T, H	0.01
Co	T, C, H	0.001
Ni	T, C, H	0.002
Cu	T, C, H	0.003
Zn	T, C, H	0.01
As	E	0.003
Se	T, E	0.0004
Mo	T, H	0.01
Ag	H, C	0.0003
Cd	H	0.001
Ba	E, C, H	0.03
Hg	E, H	3×10^{-5}
Pb	H, C	3×10^{-5}

(T = trace metal; C = concentrated by marine organism; H = heavy metal; E = exceptionally toxic)

Saturated concentrations of metals in aerated sea water of pH 7.8 - 8.2 and temperature 18 - 23°C is given below (Phillips, 1980) :

Metal	Compound added	Maximum concentration in saturated solutiion (mg/l)
Ag	$AgNO_3$	2.5
Cd	$CdCl_2$	1000
Co	$CoCl_2$	200
Cr	K_2CrO_4	Very high
Cu	$CuSO_4$	0.8
Hg	$Hg SO_4$	700
Fe	$FeCl_3$	0.005
Mo	$(NH_4)_2 MoO_4$	750
Ni	$NiCl_2$	455
Pb	$Pb(NO_3)_2$	0.7
Zn	$ZnCl_2$	2.5

In general, it is possible to distinguish five different sources from which metal pollution of the environment originates : (1) weathering of rocks, (2) industrial processing of ores and metals, (3) the use of metals and metal compounds, (4) leaching of metals from garbage and solid waste dumps, sewerages, slaughter house discharge, meat processing centres, and (5) animal and human discharges which contain heavy metals - mainly from "point" areas. Upon attempting to locate the source of metal input of receiving water bodies, a distinction is often made between diffused "non-point" and "point" sources. Essentially, rural areas are regarded as non-point sources, since the metal supply originates from vast areas (Wittmann, 1979). Johnston (1976) has classified three broad categories of marine pollutants : (i) native or natural which are not caused by man, (ii) generated by man, but not created by him and (iii) the synthetic pollutants wholly created by man. Generally, heavy metals are broadly put in the first category.

The natural sources of metals in coastal waters are through river run-off. There are 14 major, 44 medium and 162 small rivers in India (Glasby and Roonwal, 1995). The mean annual run-off is 1645 km^3 and 500 million tonnes sediments are discharged into the sea. The water and sediments fluxed into the sea is dispersed through upwelling, semi diurnal tides, waves, currents and other processes. The solid waste and garbage generated by coastal population per year is 33 million tonnes (Qasim *et al.*, 1988). In each year, 4.4 km^3 of domestic sewage and 0.44 km^3 of industrial wastes are discharged into seas off India (Glasby and Roonwal, 1995). Approximately 20,000 MLD of domestic sewage reach the coastal environment of the country mostly in untreated form (Subramanian and Abidi, 1993). Totally 100 mt of fly-ash produced in India annually, and they are the source of cadmium, aluminium and other heavy metals in the water. In India, 381,000 tonnes of pesticides and halogenated hydrocarbons are used in a year. Out of that 55,000 tonnes are used in agriculture. Use of DDT and its isomers is approximately 107,000 tonnes. The residuals in the form of trace (heavy) metals, usually find their way to the sea as their sink. In addition, metals wasted from the atmosphere through rainfall, wind blown dust and volcanic lava also add to this.

The heavy metals which occur in natural waters are lead, copper, zinc, cadmium, chromium and nickel (Dickinson, 1974 b). The first three of these are present naturally in the rivers and streams of some mining areas and all the six metals may be derived from electroplating wastes. Active mining operations may be expected to cause increase in the concentration of lead, copper and zinc in the areas where their minerals are mined and processed, owing to disturbance of the surface soil and dumping of waste from processing operations. Modern electroplating plant is designed to avoid wastage of the metal solutions used, but nevertheless some loss is unavoidable and traces of metals are discharged in the effluents from such factories and eventually find their way, to some extent into natural waters. The sources of some of the metals into the water medium are reviewed from the literature of various authors (Sittig, 1973; Ramachandran *et al.*, 1991; Forstner and Wittmann, 1983; Mohapatra, 1993; Dara, 1997) are presented below :

Elements	Sources
Al	Mining, fly-ash, municipal waste, coal, metal industry.
As	Mining, smelter plants, herbicides, sterilants, coal mining (approx. 5 μg/g coal), insecticides.
Ba	Manufacture of alloys, glass, ceramics, television picture tubes, sugar refining, lubricants in drilling oil wells, diesel fuels, explosive manufacturing unit.
Be	Combustion of coal, nuclear reactors, fluorescent lamps, alloys.
Cd	Metal industry, refining of zinc, lead, copper, electroplating, alloying, pesticides, fly-ash, petrochemicals, fertilizers, textile printing, photography, protective coatings of iron, copper, steel, cigarettes, paint, plastics, batteries, municipal waste water, leather tanning.
Cr	Chrome plating, mining, burning of coal, fuel additive, tanning agents, corrosion inhibitors, varnishes, paints, inks, explosives, wood preservatives, municipal wastes, manufacture of steel, electric cells, rubber goods, photography, pulp and paper board mills, petrochemicals, fertilizers.
Co	Alloys, turbines making, high speed tools.

Elements	Sources
Cu	Coolant water discharge, corrosion of pipe lines, minicipal drainage/sewerage, combustion of coal, mining, dredging in harbour, antifouling paints, pulp and paper board mills, fertilizers, petroleum refining, steel works foundaries, fly-ash, copper fungicides, copper bearing acid mining.
Fe	Mining, chemical industries, dye industries, fertilizers, organic chemicals, metal processing, textile mills, food canneries, tanneries, titanium dioxide production, iron and steel production, petrochemicals.
Pb	Leaded petrol, exhaust of motor vehicles, pulp and paper board mills, oil refineries, irorganic and organic chemical industries, fertilizers, steel industries, fly-ash, combustion of coal, dredging of harbours, battery plates, paints, lead oxide, ship breaking industry, photography, mining, smelting, alloys, roadside soil and dust.
Mn	Iorn and steel industries emission from welding rods, fuel additive, dry cell batteries, glass and ceramic industries, paint and varnishes, dye, fireworks, ferro-manganese, electric coils, burning of fossil fuels.
Ni	Metallurgical plant, silver refineries, industries concerned primarily with copper or brass plating, storage batteries, printing fabrics, automobile plants, electrodes, paints, pigments, combustion of oil, pulp and paper board mills, fertilizers.

Elements	Sources
Se	Fuels, ores, burning of trash - particularly paper, paints, dyes, insecticide, glass manufacturing unit, pulp and paper mill effluent/wastes, electrical and electronic industries, ceramics, rubber production, photocopiers, ink, anti-dandruff shampoos, plastics, alloys, fly-ash, refinery.
Ag	Metal alloy, porcelain, photographics, electroplating, ink manufacturing.
Sn	Plating, manufacture of alloys, reducing agent in laboratories, biocides, acaricide, antifouling agents.
Zn	Electroplating, fly-ash, combustion of coal, dredging of harbour, pulp and paper mill waste, petrochemicals, organic chemicals, fertilizers, steel work foundaries, Zn, Pb and Cu smelting industries, brass alloy manufacturing, galvanising iron and steel, dry batteries, municipal waste, pesticides, automobiles, fungicides, pigments, printing.
Hg	Chloro-alkali industries, electrical and electronic industries, plastic industry, paper and pulp industry, pharmaceuticals, fungicides, bituminous coals, anthracite coals, crude oil, residual tars, vulcanic erruption, fertilizers.

4

DISTRIBUTION OF HEAVY METALS IN COASTAL WATERS

4.1 Processes in estuaries and coastal waters

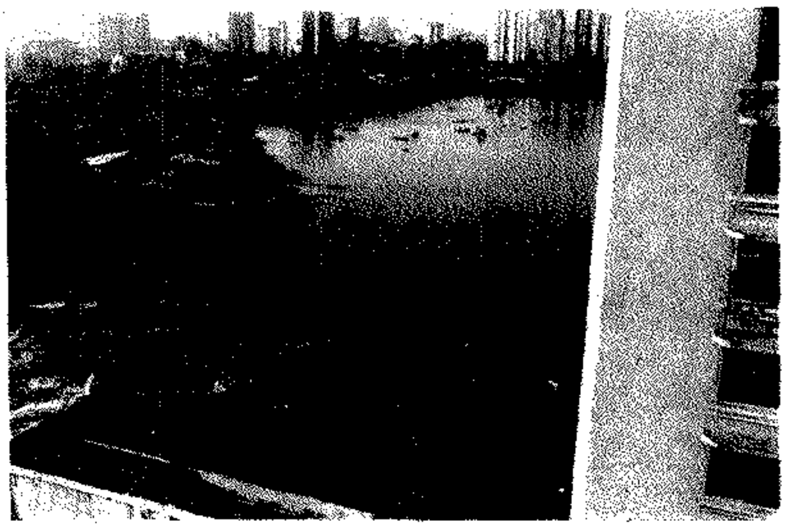
The estuaries, although not acting as major sinks, act as active geochemical areas through which the heavy metals find their way to the sea. In general, concentrations of metals are high in both soluble and particulate fractions of polluted freshwater out-falls (Phillips, 1977). As this freshwater mixes with sea water at the estuary, metals may be lost from the soluble fraction to the sediments by precipitation or to the plankton by adsorption. By this, it is meant the transfer of heavy metals from the particulate to the soluble state and *vice versa* (Salomons, 1989). The net result is the exchange of metals in soluble form from freshwater to saltwater, in particulate form mostly as inorganic nutrients, further to mostly organic products as phytoplankton in seawater (Phillips, 1980). If in an estuary a simple mixing of marine and freshwater derived heavy metals would take place, then the relationship between metal concentration and salinity would be a straight line. The mixing ratio of river and seawater determines the concentration. The curves showing the relationship between salinity and dissolved metal concentration are not straight lines, but show negative deviation in the Rhine Estuary, Netherlands (Duinker and Nolting, 1977) indicating the decrease in metal with increase of salinity. In the Scheldt Estuary, Netherlands the relationship is reverse; a release from the particulate to the dissolved state (Salomons and Forstner, 1984). The differences in geochemical processes are also reflected in metal uptake by organisms. Field observations have shown that the removal of a substantial proportion of the riverine influx of dissolved trace metals is a consistent feature of the very low salinity, high turbidity zone of the Tamar Estuary, Southwest England (Morris, 1986). Comparison of field data with the predictions of a simple sorptive equilibrium model indicates that the removal occurs through rapid uptake onto suspended particles comprising the estuarine turbidity maximum (Morris, 1986; Morris *et al.*, 1987). Copper is highly complex by carbonate and hydroxide ions in natural water and this complexity determines the concentration of copper species in solution (Pagenkopf *et al.*, 1974). Solubility is reduced in anoxic waters where H_2S is present. In organically polluted estuaries and coastal waters in the presence H_2S the metals such as Zn, Cu, Cd, Pb and Hg get precipitated. Wolfe and Rice (1972) have given a clear picture of cycling of elements in estuaries. The loss of dissolved copper, mercury and lead in association with surface active organic matter in coastal sea water is described by Wallace Jr. (1982). In coastal lagoons, embayments and other sheltered areas where water movement is restricted, pollutants rapidly build up in concentration and the effects of pollution are more pronounced (Prakash, 1981). A study conducted in North Sea showed that the removal of heavy metals takes place through settling and by incorporation of dissolved metals in biological tissues and adsorption on particulate matter (Salomons, 1989).

The process affecting heavy metals can be classified with a three layered box model comprising of the surface layers, the water column and the sediments. The sediment box is devided into two parts. The upper part is the active sediment *e.g.* the oxidised layer in which organisms are living and is in active exchange with the water column. The deeper anoxic part does not play an active role in sediment water exchange processes. In the surface layer dissolved metals are removed by uptake in biological tissues (algae) and by adsorption on particulate matter. The water column beneath the surface layer is subjected to a continuous passing through particulate matter. Part of the biogenic material decomposes in this layer which results the release of dissolved metals to the water column. These decomposition and release processes into the water column continue in the sediment surface. In addition, the environmental conditions such as pH, complexing agents cause a remobilisation

A backwater tributary turned into a highly polluted sewage in Kochi, Kerala.

Waste water discharge from Sewage Treatment Plant at Ernakulam enters an already polluted backwater area. (*Photos by* K. Rengarajan)

Mumbai city waste water pollutes the coastal water.



A highly crowded slum colony at Mumbai in a polluted coastal area.
(Photos by B. C. Mohapatra)

An inundated coastal zone with discoloured water along
Puri - Konarak Beach, Orissa.

Oozing of alkaline earth metals from Khara Nal, Maharashtra. The washings ultimately reach the sea. (*Photos by* B. C. Mohapatra)

City Waste/Sewage Treatment Plant at Puri, Orissa.

Thermal Power Station, a source of fly-ash pollution at Tuticorin Bay, Tamil Nadu. (*Photos by* B. C. Mohapatra) of heavy metals from the particulate matter (Salomons, 1989). The highly mineralised water containing calcium, potassium, sodium, magnesium and barium salts decreases the solubility of toxic substances, forming insoluble sediments with them and hence reducing their toxicity many time over (Metelev *et al.*, 1983). Phillips (1977) included stratification of water, tides and currents and the intermittent flow of industrial effluent as additional factors which may elicit changes of trace metal levels in estuarine or coastal waters.

4.2 *Seasonal variation of dissolved metals in coastal waters*

Various authors have discussed the seasonal variation of dissolved metals in inshore waters (Atkins, 1953; Knauer and Martin, 1973; Morris, 1974; Kumaraguru, 1980; Lyla, 1991; Mohapatra, 1993; Krishnakumar *et al.*, 1998). The trace metal distribution in the coastal environments to a great extent is influenced by freshwater inflow (Riley and Chester, 1971). The mercury in coastal waters of Karnataka Coast decreases during southwest monsoon starting from June (Krishnakumar *et al.*, 1998). Both the extractable and organically associated forms of copper decrease with the onset of monsoon by dilution. The input of copper which is expected to be high in the upper reaches of the river during the monsoon period, might have been affected by the increased load of suspended matter causing absorption of soluble copper in the freshwater zone and gradually released in the gradient zone, reaching maximum near the mouth (George and Sawkar, 1981). High concentration of zinc at the river mouths compared to the inter-riverine coastal areas was observed by Mohanachandran and Subramanian (1990). The decreased copper content was recorded in some estuarine environments of India in monsoon than pre-monsoon and post-monsoon (Mohapatra, 1993). Sholkovitz (1978) suggested that as much as 40% of the dissolved copper in some rivers might be removed during mixing, presumably due to flocculation with humic substances. According to Nair (1984) copper could effectively be removed from solution by adsorption on particles of hydrated ferric hydroxide and manganese oxide, the former being more abundant in coastal waters. According to the reports of Phillips (1980) the tendency of each metal to form chelates varies widely and the copper is probably the only element to exhibit significant chelate formation with humic materials in freshwater. That may also be a reason for the decreased content of copper in monsoon than other seasons.

Turekian (1971) observed that the absorbed form of metals in streams and rivers are always released to a greater or lesser extent on contact with seawater due to their displacement by major ions such as magnesium and calacium in seawater. The contribution of calcium and magnesium ions are more in higher saline areas. More salinity in the estuarine areas of India during postmonsoon and premonsoon gave a direct bearing on the abundance of heavy metals during the period (Mohapatra, 1993). During low runoff, the stagnating time of water in the estuarine nearshore zone is longer than during high runoff monsoon period. Release from sediments therefore, would be expected to have a greater dissolution of the elements in stagnating water in the estuary during low runoff (Windom *et al.*, 1983).

In the case of zinc, estuaries dominated by rivers showed higher concentration of the metal (Mohapatra, 1993). The monsoon recorded higher concentration of zinc and lead than the postmonsoon and premonsoon. The increase in zinc during monsoon in Vellar Estuary and Killai Backwater is reported by Kumaraguru (1980). The rivers during heavy monsoon empties water rich in organic content into the estuary is a probable reason for high concentration. The level of different metals in estuarine systems in different seasons has the direct bearings on the freshwater flux to the sea, location of cities and industries near the estuary, tidal fluctuations, type of estuary, etc.

4.3 Metals in coastal waters of India

Based on the published reports an attempt has been made here to review the level of heavy metals in some estuarine and coastal waters of India. The available standard values have also

TABLE 1. Heavy metals in coastal/marine waters of India (The unit is $\mu g\ l^{-1}$)

Location	Cu	Zn	Pb	Cr	Mn	Ni	Co	Cd	Hg	Fe	As	Source
Sea water	3.0	10.0	3.0	2.0	2.0	0.5	0.5	0.04	0.03	10	3	Orr and Marshal, 1969
"	–	–	–	–	–	0.228-0.693	–	0.015-0.118	0.011-0.033	–	–	Bryan, 1984
Baseline for sea water	2.0	3.0	–	–	0.3	2.0	–	0.2	–	–	–	Goldberg, 1972
Probable safe concentration	15.0	50.0	30.0	55.0	–	53.0	–	–	0.5	5.0	570	Doudoroff and Katz, 1953; Meinick *et al.*, 1956; Mckim and Benoit, 1971; EPA, 1973
WHO's standard	3.0	5.0	1.0	–	–	–	–	2.0	0.01	–	–	Qasim and Sengupta, 1981
Critical upper limit	–	–	100	–	–	–	–	10	–	–	–	Lohani, 1981
EPA recommended safe level	25	100	100	100	–	–	–	10	0.1	–	–	MPEDA, 1991 a
Favourable for shrimp farming	100	250	–	–	–	–	–	10	0.01	–	–	MPEDA, 1991 b
Arabian Sea	0.03-3.2 (1.2)	3.9-48.4 (12.3)	–	–	–	–	–	–	–	–	–	Topping, 1969
"	4.9 ± 0.3	19.2 ± 1.8	–	–	–	3.2 ± 0.3	2.2 ± 2.3	–	–	20 ± 2.3	–	Sengupta *et al.*, 1978
Lakshadweep Sea	13.3 ± 1.1	2.9 - 29.7	–	–	–	–	–	–	–	–	–	Sanzgiri and Caroline, 1979

TABLE 1 (Contd.)

Location	Cu	Zn	Pb	Cr	Mn	Ni	Co	Cd	Hg	Fe	As	Source
Bay of Bengal	2.7-6.8	2.6-15.3	–	–	–	0.8-30.3	–	0.3	0.05-0.3	–	–	Braganca and Sanzgiri, 1980; Qsim and Sengupta, 1981
Arnala Island, Maharashtra	–	–	–	–	–	–	–	–	0.02-0.1	–	–	Venkatesh *et al.*, 1989.
Bombay Harbour Bay	5.5	14.54	-	-	2.78	-	-	-	-	9.9	-	Matkar *et al.*, 1981
Karnataka Coast	-	-	-	-	-	-	-	-	0.05-1.8	-	-	Krishnakumar *et al.*, 1998
Cochin Backwater	2-40	25-165.5	ND-60.5	-	-	-	-	-	-	-	-	Mohapatra, 1993
Kali Estuary, Karwar	110	-	-	44	327	-	-	-	-	-	-	Veer *et al.*, 1992
Korapuzha Estuary, Calicut	1.5-18.5	ND-52.5	ND-8.8	-	-	-	-	-	-	-	-	Mohapatra, 1993
Mandovi-Zuary Estuary, Goa	4.5	18.7	-	-	45.2	-	-	-	-	-	ND-66.6	Zingde *et al.*, 1976
Mindhola Estuary	2.7-16	3.0-48	2.3-68	-	-	-	-	-	-	-	-	Zingde *et al.*, 1988
Saurastra Coast	5.7-8.0	10.5-11.9	-	-	8.8-10.4	2.6-3.1	0.8-8.3	-	-	-	-	Kesava Rao and Indusekhar, 1986
Point Calimere	2.0-8.0	22-40	1.5-2.5	-	-	0.7-2.0	-	0.1-0.6	-	-	-	Ramachandran *et al.*, 1991
Cuddalore marine environment	10.5-116	10-133	-	-	0.5-78.2	ND-8.0	ND-3.0	2.0-27	-	-	-	Ananthan *et al.*, 1994

Table 1 (Contd.)

Location	Cu	Zn	Pb	Cr	Mn	Ni	Co	Cd	Hg	Fe	As	Source
Ennore Creek, Madras	2.5-30	9-127	ND-141.5	-	-	-	-	-	0.0012	-	-	Joseph, 1991; Mohapatra, 1993
Madras Coast	-	-	-	-	-	5-17	-	1.4	1-1.2	-	-	Somasundaram *et al.*, 1987
Mandapam sea water	1-24	3.5-52	ND-19.0	-	-	-	-	-	-	-	-	Mohapatra, 1993
Offshore water, Tuticorin	4.0-5.0	-	2.0-7.8	-	-	-	-	0.4-2.0	0.1-0.12	-	-	Ramachandran *et al.*, 1991
Offshore water, Madras	3.2	-	5.0-6.0	-	-	-	-	0.1-0.8	0.03-0.06	-	-	"
Parangipettai marine environment	5-110	4.0-87	1.5-3.0	-	0.5-1.9	ND-5.0	ND	2.0-25	-	-	-	Ananthan *et al.*, 1994
Porto Novo	-	-	-	-	-	-	-	-	0.4	-	-	Daniel, 1987
Rusikulya Estuary, Orissa	ND-10	1.5-65	1-39.5	-	-	-	-	-	0.133-13.3	-	-	Gouda and Panigrahi, 1992; Mohapatra, 1993
Tuticorin Bay	1.5-13.0	ND-38.5	ND-31	-	-	-	-	-	-	-	-	Mohapatra, 1993
Vellar Estuary Tamil Nadu	8-26.5	25.5-95.5	-	-	-	-	-	-	-	-	-	Lyla, 1991
Kodikkarai Coast, Tamil Nadu	<9.0	<4.0	-	-	-	-	-	-	-	-	-	Pragatheeswaran *et al.*, 1988

ND = Not Detected

been tabulated for comparison and prediction of "Safe limits" in the environment (Table 1). The data presented in the Table clearly indicate that :

1. the mean values of Cu, Zn and Pb in water of almost all centres are found below the Environment Protection Agency's (EPA) safe limits except some localized pollution (Mohapatra, 1993);
2. compared to that of WHO's standard all the centres are exhibiting higher Cu, Zn and Pb;
3. mercury in the Rusikulya Estuary, Tuticorin and Madras Coast is higher than the recommended level;
4. localised pollution of cadmium found in Parangipettai and Cuddalore marine environments;
5. in Kali Estuary the chromium and copper are found to be above EPA safe level, and
6. from coastal aquaculture point of view these metals are not posing any threat in most of the estuarine areas of India.

Scientific data base for heavy metal pollution in coastal waters of India are available only for a very few locations. The available information indicates that these waters in India except few areas have not reached the alarming stage from metal pollution point of view and can be used for fish/shellfish culture. But how far this situation will continue? The planned increase in oil exploration, discharge and disposal of untreated and partly treated domestic and industrial wastes, discharge of industrial coolant waters, harbour activities, mechanised fishing activities call for an immediate establishment of a strong scientific data base through which continuous monitoring of coastal waters can be done. This will help in identifying and understanding the environmental changes and also in coastal zone management practices. Though the metals are the normal constituent of living matter essential for many life processes at low concentration, it is their excess which has to be guarded against.

5

STANDARDS AND SAFE LEVELS OF METALS IN WATER

The decision as to the quantity of toxic substances which may be discharged into a body of water at any point must be based on a knowledge of the toxicity of the substance concerned, together with a full knowledge of all the other substances already present in the receiving water and their toxicities. The recommendations go into this matter fairly thoroughly in so far as toxic metals are concerned. With the exception of lead, the various metals are more toxic or harmful to fish than to human beings. If the water is suitable for fishery with regard to the content of metals in it except lead, it will in general be suitable as a water supply. The contents of metals in the fishery, water with not less than 40 mg/l hardness should not exceed the values stated below (Dickinson, 1974 a).

Metals	Limits (mg/l)
Lead	1.0
Copper	0.1
Zinc	1.0
Cadmium	0.01
Nickel	5.0
Chromium	1.0

Requirements for discharging waste water into the biological stream {I.S. (Part I), 2490 (1974) Indian Standards Institution, New Delhi} is as follows:

Constituent	Effluent standard (mg/l except pH and temperature)
pH	5.5 - 9.0
Temperature	40°C
Suspended solids	100.0
Oil and grease	10.0
Phenols	1.0
Sulphides	2.0
BOD	30.0
COD	250.0
Total residual chlorine	1.0
Fluoride	2.0
Cd	2.0
Cu	3.0
Hg	0.01
Zn	5.0
Se	0.05
Ni	3.0
Pb	0.1
As	0.2

The tolerance limits for water quality after receiving discharges are as follows (IS 7967-1976) :

Parameters	Tolerance limits for	
	Bathing, recreation, shellfish and commercial fish culture and salt manufacturing	Harbour water
pH	6.5 - 8.5	6.5 - 9.0
Free ammonia (as N) mg/l, maximum	1.2	-
Phenolic compounds (as C_6H_5OH) mg/l, maximum	0.1	-
Dissolved oxygen, minimum	40% saturation value or 3 mg/l whichever is higher	3 mg/l
Pesticides (chlorinated hydrocarbons) (as Cl) mg/l, maximum	0.002	-

Parameters	Tolerance limits for	
	Bathing, recreation, shellfish and commercial fish culture and salt manufacturing	Harbour water
Arsenic (as As) mg/l, maximum	0.2	–
Mercury (as Hg) mg/l, maximum	0.0003	–
Oil and greasy substances (sampled in 30 cm surface layer) mg/l, maximum	0.1	10
Biochemical oxygen demand (5 days at 20°C) mg/l, maximum	5	5
Bioassay test	Not less than 90% of test animals shall survive in 96 hr test	–
Coliform bacteria MPN index per 100 ml, maximum	1000	2500

IS 7968-1976 (Indian Standards Institution, New Delhi) suggested the following values for radioactive emitters in marine waters.

Radioisotope	Maximum permissible concentration (μc/ml)
Barium 140	3×10^{-5}
Caesium 134	9×10^{-7}
Caesium 137	2×10^{-6}
Cerium 144	1×10^{-5}
Chromium 51	4×10^{-5}
Iodine 131	4×10^{-8}
Iron 59	5×10^{-8}
Nickel 63	2×10^{-5}
Phosphorus 32	2×10^{-9}
Radium 226	3×10^{-9}
Radium 228	8×10^{-9}
Ruthenium 106	2×10^{-7}
Silver 110	5×10^{-8}

Radioisotope	Maximum permissible concentration (μc/ml)
Strontium 89	3×10^{-5}
Strontium 90	3×10^{-7}
Sulphur 35	3×10^{-5}
Uranium (natural)	2×10^{-5}
Zinc 65	4×10^{-4}
Zirconium 95	1×10^{-5}

The following criteria are for evaluation of conditions for the maintenance of a well balanced warm water fish population. They are applicable at any point in the water bodies except for area immediately adjacent to outfalls (Metcalf and Eddy, Inc., 1972).

Dissolved oxygen :	Not less than 3.0 mg/l at any time.
pH :	In between 5.0 and 9.0 Preferably between 6.5 and 8.5.
Toxic substances :	Not to exceed 1/10th of the 48 hr median tolerance limit (@ LC50), except that other limiting concentrations may be used in specific cases, when justified on the basis of available evidence and approved by the appropriate regulatory agency. In the case of heavy metals such as copper, zinc and lead not to exceed 1/100th of the 96 hr LC50 (Mohapatra and Rengarajan, 1995). The environmental standards for chromium are usually set on the basis of hexavalent chromium. EPA guidelines indicate that lead concentrations in both marine and freshwater systems should not exceed 1% of the 96 hr TLm (@ 96 hr LC50) for sensitive species (EPA, 1976).

The median tolerance limit (≅ LC50) of some metals to fish and their probable safe concentrations are listed below with the source :

Element	TLm (mg/l)	Probable safe conc. (mg/l)	References
Fish			
Al	0.3 (24 hr)	≤ 0.1	McKee and Wolf, 1963
As	1.1-2.2 (48 hr)	≤ 0.7	Meinick *et al.*, 1956
Cr	5-118 (96 hr)	≤ 0.05	EPA, 1973; Pickering and Henderson, 1966
Cu	3-7 (48 hr)	≤ 0.015	McKim and Benoit, 1971
Fe	0.1-10 (24-48 hr)	≤ 0.03	Doudoroff and Katz, 1953
Pb	1-7 in soft water (96 hr)	≤ 0.03	Pickering and Henderson 1966; EPA, 1973;
Hg	1.0 (96 hr)	0.0005	EPA, 1973
Ni	5-54 (96 hr)	≤ 0.03	Pickering and Henderson 1966; EPA, 1973; Nebekar *et al.*, 1985
Zn	0.87-33 (96 hr)	≤ 0.05	Pickering and Henderson, 1966; EPA, 1973; Cope, 1978; Woltering, 1984
Shellfish			
Cd	0.71 (96 hr)	0.0072	Devi, 1996 a
Hg	0.257 (96 hr)	0.0026	Devi, 1996 b

The effects of different concentrations of individual toxicants and the influence of the varying physico-chemical conditions of the environment upon the toxicity have been extensively studied by organisations in various parts of the world. Most of this work has involved tests with fish (Owens, 1970). A number of fish are exposed to various concentrations of the toxicants for a given length of time and the median period of survival of the fish at a given concentration of toxicant is determined. Generally, a threshold concentration is observed - this is the region where a small reduction in the concentration of the toxicant results in a very large increase in the survival time of the fish. This is used to decide the concentration of the particular toxicant which can be accepted by the fish and to help determine the consent conditions for the discharge. It is expected that a fish toxicity test will be used increasingly by the Pollution Controlling Authorities in the future, especially when unidentified toxicants are present. While this procedure tells whether adult fish will survive in the water/medium, it does not give whether or not the conditions would be suitable to support a good fishery, for example it does not give which fish will mature and breed, nor whether the eggs will hatch, nor does it give information on adverse sub-lethal effects. Nevertheless, these short-term tests must still be accepted in order to screen the very large numbers of chemical compounds being produced and to obtain a measure of their possible effects under a variety of conditions, though at the same time suitable steps should be taken to minimise errors of extrapolation.

For evaluating the toxic effects of any pollutant and for comparing the information regarding to toxicity of different chemicals, a measure called LD50 ($\cong$ LC50) is generally used. These values are specific to the species studied, duration of exposure, mode of exposure and generally under certain dietary and environmental conditions. Obviously the smaller the LD50 ($\cong$ LC50) values, the more toxic the chemical.

The safe application rate (SAR) of a pollutant is determined by multiplying SAFE (safe application factor equation) by LC50 (48 hr or 96 hr) and SAFE is estimated by dividing LC0 (the maximum concentration at which all survived for 96 or 168 hr) by LC100 (the minimum concentration at which all died in 96 or 168 hr) (Basak and Konar, 1977). The LC0 and LC100 can be estimated from the regression equations ($y = a + bx$) used for fitting "best-fits" (*i.e.*, response curves) for concentrations verses percentage of mortality of test animals (Mohapatra and Rengarajan, 1995).

6

DISTRIBUTION OF HEAVY METALS IN COASTAL SEDIMENTS OF INDIA

Heavy metals, the conservative pollutants once added to the aquatic environments prevail for ever. On dilution in water, certain amount of metals sinks to the bottom and settle alongwith sediments. The concentration found in sediments varies according to the rate of trace metal deposition, the rate of particle sedimentation, the particle size and nature, and the presence or absence of organic material (Phillips, 1977). The distribution of heavy metals in particulate matter and in sediments is dominated by mixing processes between river discharge materials and sea-derived (fairly uncontaminated) particulates. The mobilisation of metals from the particulates to the dissolved state is caused by desorption or by dissolution (Wittmann, 1979).

Relatively high concentration of trace elements in the coastal sediments near the cities and harbours are attributed to the discharge of large amount of sewage and wastes (Venugopal *et al.*, 1982; Nammalwar *et al.*, 1985; Pragatheeswaran *et al.*, 1986; James *et al.*, 1986; Mohapatra, 1993). Holmes (1986) reported the oxygen poor zone in the water column near the sediment-water interface in the harbour at Corpus Christi, Texas. This causes the chalcophilic metals such as copper, zinc, lead, etc. to precipitate from the water resulting to settlement of metals in high concentrations in the sediments particularly near the outlets of the industrial area. Studies of Mohanachandran and Subramanian (1990) revealed high concentration of copper and zinc at the river mouths compared to the area on the river side from the mouth. The possible reasons attributed by them are : (i) the river carries sediment with iron content which can act as scavenger or carrier of metals and (ii) anthropogenic contributions. Coastal grained sediments contain lesser amount of heavy metals.

TABLE 2. Heavy metals in coastal sediments of India [The unit is $\mu g\ g^{-1}$ dry wt except for iron (%)]

Location	Fe	Mn	Cu	Zn	Ni	Co	Cd	Hg	Pb	Cr	Source
Northern half of western continental shelf, India	-	500-1000	-	-	50-100	-	-	-	-	-	Murty *et al.*, 1978
Ashtamudi Estuary, Kerala	0.12-39	-	15-154	38.2-115.2	9.0	-	-	0.001-0.37	67-92	-	Nair *et al.*, 1987
Vembanad Lake, Kerala	0.22-9.6	30-898	ND-100	-	7.0-60	17-82	-	-	-	-	Murty and Veerayya, 1981
Cochin Backwater	-	40.2-41.6	36.9	409.7	10.1-14.6	6.0-12.6	-	-	51	-	Venugopal *et al.*, 1982; Mohapatra, 1993
Korapuzha Estuary, Calicut	-	-	16.7	28.5	-	-	-	-	11.8	-	Mohapatra, 1993
Kali Estuary, Karwar	-	185.7	7.02	-	-	-	-	-	-	14.1	Veer *et al.*, 1992
Arnala Island, Maharashtra	-	-	-	-	-	-	-	0.02-0.39	-	-	Venkatesh *et al.*, 1989
Bombay Harbour Bay	7.3	936.8	210.9	180.4	-	-	-	-	-	-	Matkar *et al.*, 1981
Off Bombay	-	-	-	-	-	-	ND-80	-	ND-350	-	Qasim *et al.*, 1988
Thane Creek, Bombay	-	-	-	-	-	-	-	0.18-2.4	-	-	Patel and Chandy, 1988
Narmada Estuary	8.9	1077	136	140	81	-	-	-	-	-	Borole *et al.*, 1982
Tapti Estuary	7.6	1125	128	125	70	-	-	-	-	-	"
Karnataka Coast	-	-	3.1-157	1.9-72	-	-	N.D.-2.13	N.D.-0.203	4-112.5	-	Krishnakumar *et al.*, 1998

Table 2 (Contd.)

Location	Fe	Mn	Cu	Zn	Ni	Co	Cd	Hg	Pb	Cr	Source
Mindhola River Estuary	-	435-1253	73-213	63-369	76-162	-	-	-	4.0-67	-	Zingde *et al.*, 1988
Ganges Estuary	4.2	732	44	151	49	-	-	1.4	32	98	Sasamal *et al.*, 1987; Subramanian *et al.*, 1988
Rusikulya Estuary, Orissa	-	-	8.3	9.7	-	-	-	0.05-4.96	12.6	-	Gouda and Panigrahi, 1992; Mohapatra, 1993
"	-	-	-	-	-	-	-	1.6-192	-	-	Panda *et al.*, 1990
Godavari Estuary	7.6	1294	119	-	91	-	-	-	5.0	128	Subramanian *et al.*, 1985; Biksham and Subramanian, 1988
Krishna Estuary	10	6978	69	1482	149	-	-	-	4.0	174	Subramanian *et al.*, 1985
Ennore Creek, Madras	-	-	45.2	112.8	-	-	-	0.6	18.1	-	Joseph, 1991; Mohapatra, 1993
Off Madras Coast and Visakhapatanam Coast	1.05-5.57	196-806	24-180	62-106	-	-	-	ND-30	-	-	Pragatheeswaran *et al.*, 1986
Bay of Bengal	3.9	529	26	-	64	-	-	0.2-5.25	-	84	Sarin *et al.*, 1979; Sasamal *et al.*, 1987

TABLE 2 (Contd.)

Location	Fe	Mn	Cu	Zn	Ni	Co	Cd	Hg	Pb	Cr	Source
Cauvery Estuary	3.4	1310	33	75	379	-	-	0.12	38	229	Subramanian *et al.*, 1989
Parangipettai Coast	-	68.0-232.7	55.5-165	26.5-83.3	10-35	5.0-20	1.5-8.34	-	-	-	Ananthan *et al.*, 1994
Cuddalore Coast	-	71.0-171.5	105.5-190	82.8-203.5	10-15	5.0	0.95-4.1	-	-	-	"
Kodikkarai Coast	-	-	40-75	450-1100	-	-	-	-	-	-	Pragatheeswaran *et al.*, 1988
Mandapam Coast	-	-	1.6	3.0	-	-	-	-	4.6	-	Mohapatra, 1993
Tuticorin Bay	-	-	8.7	4.9	-	-	-	-	8.0	-	"
Southeast Coast	1.1	337	17	62	-	-	2.7	0.12	53	138	Mohanachandran and Subramanian, 1990

ND = Not Detected

For many of the heavy metals seasonal differences are reported. Monsoon recorded higher copper, zinc and lead content in sediments than the dry seasons (Mohapatra, 1993). During the monsoon the estuary carries all the washouts from catchment areas which are rich in organic content. The high organic content encourage the mobilisation processes and contribute to the variations of metals (Remani *et al.*, 1990; Arzul and Maguer, 1990). Murty and Veerayya (1981) reported that copper bears significant relationship with organic matter of the sediments. With a few exceptions, higher concentration of elements are associated with the silt-clay fractions of sediments. The estuarine environments are favourable for the formation of colloids of iron and manganese oxides derived with freshwater runoff and their flocculation. It is therefore considered possible that, part of these elements might be incorporated into the sediments in association with these hydroxides through absorption. Kumaraguru (1980) recorded increased levels of copper and zinc during monsoon season in Vellar Estuary and Killai Backwater, Tamil Nadu. In the same Vellar Estuary, Lyla (1991) recorded the increased level of copper and zinc in sediment in monsoon followed by postmonsoon and premonsoon. According to Holmes (1986) during the dry seasons when the water is more stagnant, zinc and cadmium which are introduced to the system are concentrated in the oxidizing surface waters. Ultimately the deposit of metals to the sediment is reduced, thus, reducing their levels in the sediment in postmonsoon and premonsoon.

Based on available information and work of the authors, an attempt has been made here to review the status and distribution of heavy metals in coastal sediments of India (Table 2). This will serve as a mini date bank of heavy metals for our coastal sediments.

7

ACCUMULATION OF HEAVY METALS IN MARINE ORGANISMS

7.1 Processes and accumulation in different animals

Marine organisms have the ability to accumulate trace elements from the sea water. In sea water, the uncomplexed heavy metal ions may not be predominant (Bruland, 1983), but several reports show that this form of heavy metals are available to organisms which accumulate (Zamuda and Sunda, 1982; Rainbow, 1985). Cations in general have an affinity for living matter related to valency in the following manner : Tetra and trivalent elements > divalent transition elements > divalent group II A metals > univalent group I metal. Among anions the affinity for living materials is nitrates > trivalent anions > divalent anions > univalent anions. Generally, higher accumulation of heavy metals by estuarine and marine fishes and shellfishes pose a threat to the use of these resources as human food.

The use of pelecypod bivalves as sentinel animals in pollution monitoring programme are well known. These species reflect the concentration of heavy metals in the surrounding medium. These organisms not only concentrate metals from water allowing inexpensive and relatively simple analysis, but they may also represent a moving time - average value for the relative biological availability of metals at each site studied (Phillips, 1977). According to Rajan *et al.* (1991) a significant positive correlation is established between zinc concentration in body tissues of *Meretrix casta* and ambient medium in the Vellar Estuary. The bivalves are filter feeders and thus obtain trace metals not only from food and from solution, but also from the ingestion of inorganic particulate material (Moore, 1971). Cunningham and Tripp (1975) found a faster uptake of mercury in smaller individuals of *Crassostrea virginica* than in larger individuals. Patel and Chandy (1988) reported seasonal distribution of mercury in the soft tissues of *Anadara granosa* from Thane Creek. In postmonsoon (Oct. - Jan.) the concentration was found more in tissues followed by premonsoon (Feb. - May) and monsoon (June - Sept.). In soft tissues of *Marcia recens* (Pelecypoda) copper accumulation varied statistically in different seasons (Muralidharan and Raja, 1997). The accumulation of Cu, Pb and Zn was higher in females than males in *M. recens*. Metals such as Cd, Cu, Zn, Fe and Mn in the kidneys, hepatopancreas, gills, mantle and muscles of scallops collected in the Amur and Vostok Bays were higher in winter and lower in summer. Concentrations of all the metals decrease in kidneys during prespawning period and in hepatopancreas during the spawning period (Luk-Yanova and Martem-Yanova, 1996). A definite seasonal variation with an increased metal (Zn, Cu, Pb, Cd and Hg) load during the monsoon period and decreased level during the summer period in *Perna viridis* and *Crassostrea madrasensis* in southeast coast of India is reported by Senthilnathan *et al.* (1998). Salinity of the media was found to play an important role in the accumulation of metals in tissue. A linear relationship was found between the metal level in the tissues and that in the dissolved fraction. Fowler and Oregioni (1976) found differences between each metal in terms of the amount of their seasonal fluctuation in *Mytilus galloprovincialis*. The ratio between the seasonal maximum and the seasonal minimum concentration was greatest for chromium (factor of 8.8) and least for zinc (factor of 2.0). These differences must be related to differences in the biological half-lives of metals in mussels; in general, it appears that metals have shorter half-lives in bivalves than in macroalgae and the time-integration capacity of bivalves is therefore, less than that of macroalgae.

Zinc and cadmium are more bioavailabe to invertebrates at lower salinites (McLusky *et al.*, 1986). The moulting of crustaceans temporarily increases the rate of uptake of metals into the body, presumably in correlation with a temporary increase in body surface permeability prior to the tanning and/or calcification of new cuticle (Nugegoda and Rainbow, 1988). The essential metal zinc and the non-essential metal cadmium are reabsorbed into the body of the prawn *Palaemon elegans* before ecdysis (White and Rainbow, 1986). Metals detoxified in granules in the hepatopancreas or caeca of malacostracan crustaceans, for example lead in *Carcinus maenas* (Hopkins and Nott, 1979) or copper in amphipod *Corophium volutator* (Icely and Nott, 1980), will be released into the lumen of the alimentary tract when the epithelial cells complete their cell cycle. Decapod crustaceans regulate body concentrations of the essential metals zinc, copper and manganese, balancing metal uptake by varied rates of metal excretion (White and Rainbow, 1982; Nugegoda and Rainbow, 1988).

Copper is an essential component of haemocyanin, the respiratory pigment of certain molluscs and crustaceans. In decapod crustaceans, the concentration of haemocyanin in the blood falls at the time of the moult (Engel, 1987). This fall is usually interpreted to indicate that haemocyanin is broken down releasing copper, some of which stored temporarily in the hepatopancreas, possibly detoxified by binding as copperthionein. The metal concentration is also affected by the weight of the body tissue present. The rate of growth of an invertebrate may be so high that growth "dilutes" the metal content, itself increasing with time, preventing any increase in metal concentration.

Teleosts assimilate metals from both food and solution. The uptake of metals from solution may occur across the body surface (particularly the gills) or across the gastro-intestinal wall after drinking. The relative amounts of metal contributed by each route are uncertain, although the uptake of metal from food probably predominates. The situation may vary with the species of fish and with the metal considered. For example, estuarine species may be exposed to higher concentations of metals in solution than is normal in a marine situation. Variation with metal must occur, because of the variation in concentration factors for metals in phytoplankton and other fish foods, and because of the varying ratios of metals in the soluble and particulate phases of water. Teleosts probably do not respond directly to metals associated with inorganic particulate material, but they may respond indirectly to this fraction if preying substantially on filter-feeding organisms which do derive metals from this fraction.

Published data on the concentrations of mercury in teleosts suggest that certain species are capable of acting as efficient indicators of pollution by this element. According to Krishnakumar and Pillai (1990) the sequence of mercury levels in different biota is as follows : sardine < squid < crab < prawn < mackerel < seaweed < mussel < oyster. The order of metal accumulation in *Perna viridis* and *Crassostrea madrasensis* was found to be Zn > Cu > Pb > Cd > Hg in southeast coast of India (Senthilnathan *et al.*, 1998). The accumulation of Cu, Zn, Cd and Pb was found in different tissues of *C. madrasensis* in the order of gill > mantle > adductor muscle (Senthilnathan and Balasubramanian, 1998).

Generally fishes showed higher levels of metals if they feed at the bottom of the system *i.e.* detritus feeders (Zingde *et al.*, 1976; Mohapatra, 1993). In the process of feeding by sucking up the surface layer of the mud or by grazing on the rock surfaces the transfer of mineral particles into the system along with food take place. The detritus feeders are exposed to more quantities of metals than fishes with pelagic feeding habits.

Ranges of concentrations of some essential and non-essential heavy metals in zooplankton, crustaceans, bivalves and in the muscles of certain fishes from the North Indian Ocean are given by Kureishy (1985). Accumulation of different heavy metals in marine organisms is given in Table 3.

TABLE 3. Accumulation of different heavy metals (ppm dry wt./ppm wet wt.) in marine organisms

Species	Place	As	Cd	Cu	Cr	Fe	Mn	Ni	Hg	Zn	Pb	Source
Crassostrea spp.	Goa estuarine waters	-	-	175-728	-	-	-	-	-	upto 2800	-	Zingde *et al.*, 1976
Liza parsia, *Etroplus suratensis* *Rastrelliger kanagurta*	"	-	-	14.9-32.5	-	-	-	-	-	-	-	"
Marine fishes	"	0.3-12.6	-	-	-	-	-	-	-	7.5-76.5	-	"
Portunus pelagicus	"	upto 25.0	-	-	-	-	-	-	-	-	-	"
Arius sp.	Bombay Harbour Bay	-	-	0.88-4.35	-	3-11.5	1.41-3.74	-	-	9.42-30.55	-	Matkar *et al.*, 1981
Ascelis indicus (prawn)	"	-	-	11.2	-	15.0	-	-	-	11.15	-	"
Scylla serrata (crab)	"	-	-	23.6-34.0	-	114.2	4.76	-	-	upto 60.7	-	"
Teleosts	-	-	-	-	-	-	-	-	-	6-400	-	Eisler, 1981
Anadara granosa	Thane Creek	-	-	-	-	-	-	-	0.64 - 0.82	-	-	Patel and Chandy, 1988
Boleopthalmus boddaerti	-	-	-	-	-	-	-	-	0.63 - 0.14	-	-	"
Perna viridis	Karnataka Coast	-	0.16-0.81	1.5-128	-	-	-	-	ND-0.02	11.1-70.5	0.31-2.52	Krishnakumar *et al.*, 1998
Crassostrea cucullata	"	-	1.47-2.76	21.2-201	-	-	-	-	ND-0.57	31-703	0.3-3.98	"
Meretrix casta	"	-	0.52-0.89	3.94-18.4	-	-	-	-	ND-0.01	11.1-34.9	1.1-2.8	"
Sardinella longiceps	Karwar Coast	-	0.76±0.18	1.06±0.16	-	-	1.21±0.40	-	-	5.28±1.07	ND	Krishnakumar *et al.*, 1990

TABLE 3 (Contd.)

Species	Place	As	Cd	Cu	Cr	Fe	Mn	Ni	Hg	Zn	Pb	Source
Rastrelliger kanagurta	Karwar Coast	-	0.66±0.08	1.16±0.16	-	-	0.42±0.44	-	-	6.66±0.75	0.006 ±0.002	Krishnakumar *et al.*, 1990
Loligo duvaucelli (Squid)	"	-	0.66±0.08	7.08±0.99	-	-	1.73±0.10			12.54±2.2	0.142±0.04	"
Penaeus merguiensis	"	-	0.38±0.09	14.63±2.5	-	-	0.98±0.1			11.52±2.08	0.208±0.01	"
Parapenaeopsis stylifera	"	-	0.83±0.13	18.63±2.21	-	-	0.23±0.07			26.61±3.9	0.092±0.01	"
Portunus pelagicus	"	-	1.29±0.48	20.06±2.04	-	-	1.81±0.23			21.55±2.95	0.56±0.14	"
Oyster	"	-	1.82±0.4	38.6±13.6	-	-	4.6±1.35			91.1±51.2	0.308±0.07	"
Mussel	"	-	0.27±0.12	2.28±0.79	-	-	7.26±1.05			14.41±1.9	0.53±0.35	"
Sea weed	"	-	0.57±0.23	4.22±1.7	-	-	8.57±5.31			1.38±0.76	0.95±0.59	"
Marcia recens (Plecypoda)	Madras Coast	-	0.66±0.71	8.85±3.86	-	-			1.41±1.19	38.76±9.63	4.83±2.06	Muralidharan and Raja, 1997
Oysters	North Indian Ocean	-	-	-	-	-	-	-	-	-	1.0	Kureishy, 1985
Mussels	"	-	-	-	-	-	-	-	-	-	1.31	"
Prawns	"	-	-	3.5-24.0	-	-	-	-	-	-	1.0	"
Marine biota	Madras Coast	-	2.0-7.5	78-530	-	-	-	0.1-22	0.08-0.9	5.0-1200	0.18-25	Daniel, 1987
"	Point Calimere	-	0.02-0.025	0.05-0.15	-	-	-	0.01-0.02	-	1-14	0.02-0.025	Natarajan, 1987
29 Marine fishes and 3 shellfishes	Ennore Estuary landing centre	-	-	-	-	-	-	-	0.01-0.48	-	-	Joseph and Srivastava, 1993

TABLE 3 (Contd.)

Species	Place	As	Cd	Cu	Cr	Fe	Mn	Ni	Hg	Zn	Pb	Source
Shrimps and prawns	Pacific	-	0.1-0.53	10.2-19.5	0.5-3.7	-	-	0.1-0.67	-	39.8-52.9	0.6-1.47	Harding and Goyette, 1989
Perna viridis	Gulf of Thailand	-	0.88-6.84	9.38-15.63	0.16-1.12	178.9-1000	-	0.61-1.53	0.12	61.1-76.47	-	Phillips and Muttarasin, 1985
Crassostrea commercialis	"	-	2.05-3.82	100-180.9	0.24-0.59	105-147.4	-	0.2-0.53	0.1	571.4-1047.6	-	"
Anadara granosa	"	-	1.33-6.47	4.89-8.75	0.18-0.56	385-1000	-	0.37-1.41	0.1	68.4-125	-	"
Paphia undulata	"	-	0.25-0.8	4.55-7.37	0.32-1.5	442.1-1055.6	-	0.55-1.39	0.1	42-57.9	-	"
Oysters	Philippines	-	0.064-0.18	14.87-42	-	-	-	-	0.057-0.073	25.6-201	0.037-0.161	Gomez and Deocadiz, 1987
Mussels	"	-	0.045-0.4	2.38-5.0	-	-	-	-	0.038-0.093	10.4-23.7	0.078-0.122	"
Tilapia spp.	Jakarta Bay	-	0.02-0.03	0.33-0.68	-	-	-	-	0.02	0.3-9.04	0.09-0.68	Soegiarto, 1987
Rastrelliger spp.	"	-	0.02-0.03	0.66-0.69	-	-	-	-	0.02-0.114	0.63-9.63	0.11-0.16	"
Penaeus spp.	"	-	0.02	1.7-3.2	-	-	-	-	0.05-0.43	11.31-15.96	-	"
Cuttlefish and cockles	"	-	0.02-0.03	0.08-1.49	-	-	-	-	0.08-0.5	11.74-13.96	-	"
Anadara spp.	"	-	0.04-0.25	0.34-2.7	-	-	-	-	0.06-0.25	14.23-19.85	0.68	"
Mercenaria mercenaria	United Kingdom	-	-	12.9-32.0	-	107.2-240.8	-	-	-	50.5-131.3	-	Phillips, 1980

7.2 *Accumulation in fish tissues*

In *Liza parsia* higher copper content was noticed in liver followed by kidney, intestiine, gills, ovary, muscle and skin in that order (Mohapatra, 1993). The concentration levels of copper, zinc, manganese and iron have been determined in marine fishes from Cochin area. The metal showed increased levels in gills and alimentary canal compared to the muscle (Nair *et al.*, 1997). According to Jaffer and Ashraf (1988) the level of copper was found minimum in the muscle of *Pampus argenteus* and *Formio niger*, while in liver and kidney the levels were high. Higher content of copper in liver of *Ictalurus nebulosus* was reported by Benedetti *et al.* (1981) in *Barbus grypus*. There are several reports available in support that liver accumulates more copper. Gill metallothionein binds only a very small amount of copper and zinc compared to liver (Noel-Lambot *et al.*, 1978). According to Phillips (1977) copper tends to concentrate in soft organs such as liver and kidney of fish, but gonad contains extremely low concentrations of all metals other than zinc. Only the axial muscle concentrates very little amount of all heavy metals (Phillips, 1977). In many cases no good relations for copper, lead and zinc were found between the tissues and abiotic factors such as metals in water and sediment (Wilson *et al.*, 1981; Jaffer *et al.*, 1988; Harding and Goyette, 1989; Yong and Harvey, 1989; Mohapatra, 1993). According to Yong and Harvey (1989) the absence of relation between concentrations of Fe, Zn, Cu in liver, kidney and muscle tissues and fish size ($P < 0.05$) implies that these metals are homeostatically controlled. The absence of correlation may reflect either regulation by the fish or limited input from the environment (Milner, 1982). Generally no seasonality in copper, lead and zinc concentrations in different tissues of *L. parsia* could be noticed (Mohapatra, 1993). In marine pollution studies there is little evidence of correlation between measured levels of trace elements (except mercury) in fish tissues and environmental levels

(Windom *et al.*, 1973; Eustace, 1974). This has been attributed to the mobility of fish with the localised nature of metal contamination in the sea.

The higher content of zinc is recorded in ovary followed by liver, skin, intestine, gills, kidney and muscle in that order in *L. parsia* (Mohapatra, 1993). From all the reports it is found that muscle tissue accumulates less zinc. Among the teleosts, along with the gonad, the specific site of zinc concentration is viscera (Eisler, 1981).

Lead is a non-essential element. The higher the concentration of lead to which *Crangon crangon* is exposed, the more it accumulates, showing no evidence of regulation (Amiard *et al.*, 1985). Lead will bind to metallothionein, but also has an affinity (probably higher) for other metabolic ligands, often associating with deposited inorganic granules with high concentrations of calcium (Brown, 1982). Higher content of lead was recorded in gills followed by intestine, ovary, kidney, liver, skin and muscle in that order in *L. parsia* (Mohapatra, 1993). According to Eisler (1981) hard tissues such as bone is supposed to be the place of lead accumulation. Distinct tissue specific accumulation rates were found in *Gillichthys mirabilis* : gill and intestine accumulated the highest amount of lead while liver and muscle accumulated the least (Somero *et al.*, 1977). Brooks and Rumsey (1974) found that in general, zinc, cadmium, copper and iron are concentrated in soft organs of teleosts such as liver, kidney, spleen, heart, gonads whereas lead and manganese are concentrated in bony organs such as gill, backbone and tail. The turn-over of lead in the mucus covered tissues such as gills and intestine is a result of lead complexion with mucus (Somero *et al.*, 1977).

Liver and gill accumulate lesser quantity of mercury than muscle in *Tilapia* sp. (Ayyadurai and Krishnaswamy, 1989). As a high-ranking predator the pike exhibits high concentration of

TABLE 4. Accumulation of heavy metals (ppm dry wt./ppm wet wt.) in different tissues of marine organisms

Element	Species	Place	Liver	Gill	Muscle	Skin	Kidney	Intestine/ Gut	Gonad	Whole body	Source
As	*Carcharias sorrakowah*	Goa estuarine and coastal waters	23.2	15.2	10.8	-	-	-	-	-	Zindge *et al.*, 1976
Cd	*Liza macrolepis*	Adyar Estuary	0.78	0.74	1.55	-	-	-	-	-	Nammalwar, 1985
	Marine fishes	Marine environment of India	0.34	0.31	0.7	-	-	-	-	-	Qasim and Gupta, 1980
	Fishes	North Indian Ocean	20.18	0.42	0.59	-	9.02	-	1.25	-	Kureishy, 1985
	Anguilla anguilla	Lower Medway Estuary, UK	0.15-0.59	-	0.08-0.5	-	-	-	-	-	Wharfe and Van Den Broek, 1977
	Gadus morhua	Gdansk Bay	0.19	0.56	0.05	-	0.45	0.04-0.06	0.07	0.07	Szefer *et al.*, 1990
	Mya arenaria	"	-	0.4	0.36 (Mantle)	-	-	0.65	0.2	0.4	"
	6 Marine fishes	Aqaba, Jordan	ND-6.3	ND-3.6	ND-4.0	-	-	-	1.3-4.8	-	Wahbeh and Mahasneh, 1987
	Merlangus merlangus	Lower Medway Estuary	0.13-0.18	-	0.1-0.28	-	-	0.08-0.21	-	-	Wharfe and Van Den Broek, 1977
	Platichthys flesus	"	0.15-0.22	-	0.06-0.07	-	-	0.13-0.23	0.08	-	"
	Pleuronectes platessa	"	0.16-0.21	-	0.054-0.15	-	-	0.2-0.25	-	-	"
	Pagothenia borchgrevinki	Antarctica	0.3-2.46	-	0.01-0.04	0.04	-	-	0.04-0.43	0.01-0.12	Honda *et al.*, 1983
Co	*Gadus morhua*	Gdansk Bay	0.03	0.35	0.05	-	ND	0.05-0.12	0.09	0.07	Szefer *et al.*, 1990
	Mya arenaria	"	-	0.6	1.0 (Mantle)	-	-	0.5	0.41	0.7	"
	6 Marine fishes	Aqaba, Jordan	1.5-6.9	ND-6.1	0.2-4.3	-	-	-	0.3-6.1	-	Wahbeh and Mahasneh, 1987

TABLE 4 (Contd.)

Element	Species	Place	Liver	Gill	Muscle	Skin	Kidney	Intestine/ Gut	Gonad	Whole body	Source
Cr	*Mugil cephalus*	Kali Estuary	-	8.78	8.65	-	-	-	-	8.28	Veer *et al.*, 1992
	Silago sihama	"	-	16.83	6.63	-	-	-	-	11.01	"
	Leiognathus brevirostris	"	-	10.22	6.52	-	-	-	-	9.42	"
	Gerromorpha setifer	"	-	18.54	6.05	-	-	-	-	12.29	"
	6 Marine fishes	Aqaba, Jordan	0.6-2.4	0.7-2.8	ND-1.5	-	-	-	ND-1.1	-	Wahbeh and Mahasneh, 1987
Cu	*Mugil cephalus*	North Atlantic	-	-	1.9	-	-	-	-	-	Windom *et al.*, 1973
	"	Kali Estuary	-	3.93	5.27	-	-	-	-	5.46	Veer *et al.*, 1992
	Liza macrolepis	Adyar Estuary, Madras	8.9	1.63	0.6	-	-	-	-	-	Nammalwar, 1987
	"	Ennore Estuary, Madras	6.76	2.83	2.5	-	-	-	-	-	"
	Liza parsia	Korapuzha Estuary, Calicut	19.2	12.0	5.2	5.4	35.8	7.3	8.0	-	Mohapatra, 1993
	"	Cochin Backwater	15.1	8.9	4.1	6.1	12.3	8.3	4.5	-	"
	"	Tuticorin Bay	129.4	4.2	8.8	5.8	21.7	22.6	7.2	-	"
	"	Mandapam waters	52.2	4.9	5.8	5.4	27.2	5.2	4.4	-	"
	"	Ennore Creek, Madras	58.1	7.8	6.3	5.6	16.2	7.6	6.7	-	"
	"	Rusikulya Estuary, Orissa	5.7	7.7	6.3	3.9	12.5	8.5	13.3	-	"

Table 4 (Contd.)

Element	Species	Place	Liver	Gill	Muscle	Skin	Kidney	Intestine/ Gut	Gonad	Whole body	Source
	Pagothenia borchgrevinki	Antarctica	0.92-5.88	-	0.17-1.39	0.55-0.65	-	-	0.7-2.22	0.38-1.07	Honda *et al.*, 1983
	Pleuronectes platessa	Medway Estuary, U.K.	1.5-4.2	-	0.5-1.7	-	-	1.8-3.2	-	-	Wharfe and Van Den Broek, 1977
	Platichthys flesus	"	7.4-23	-	0.3-1.3	-	-	1.0-4.8	2.4	-	"
	Merlangus merlangus	"	1.3-3.5	-	0.2-1.0	-	-	0.5-2.5	-	-	"
	Anguilla anguilla	"	5.0-36.9	-	0.3-1.0	-	-	-	-	-	"
	Gadus morhua	Gdansk Bay	1.2	0.91	0.24	-	1.5	0.51-0.85	0.41	0.29	Szefer *et al.*, 1990
	Mya arenaria	"	-	2.5	2.0 (Mantle)	-	-	3.0	9.0	3.1	"
	Silago sihama	Kali Estuary	-	9.72	5.15	-	-	-	-	7.74	Veer *et al.*, 1992
	Leiognathus brevirostris	"	-	6.46	3.77	-	-	-	-	6.86	"
	Gerromorpha setifer	"	-	12.53	4.37	-	-	-	-	11.83	"
	6 Marine fishes	Aqaba, Jordan	6.4-19.2	ND-9.6	ND	-	-	-	ND-5.3	-	Wahbeh and Mahasneh, 1987
Fe	*Gadus morhua*	Gdansk Bay	8.8	43	2.8	-	115	14.6-17.5	8.1	5.4	Szefer *et al.*, 1990
	Mya arenaria	"	-	100	5100 (Mantle)	-	-	140	390	2100	"
	6 Marine fishes	Aqaba, Jordan	413.3-1253.3	80-320.4	35.6-71.2	-	-	-	88.9-160	-	Wahbeh and Mahasneh, 1987
	Pagothenia borchgrevinki	Antarctica	10-114	-	1.42-5.95	5.52-5.88	-	-	6.4-13.8	4.04-9.25	Honda *et al.*, 1983

TABLE 4 (Contd.)

Element	Species	Place	Liver	Gill	Muscle	Skin	Kidney	Intestine/ Gut	Gonad	Whole body	Source
Hg	Fishes (Marine)	Indian Ocean	0.04	0.06	0.1	-	-	-	-	-	Kureishy *et al.*, 1980
	Fishes	North Indian Ocean	0.01	0.016	0.07	-	0.015	-	0.015	-	Kureishy, 1985
	Fishes	Rusikulya Estuary	0.19-1.15	-	0.17-22.5	-	-	-	-	-	Gowda and Panigrahi, 1992
	Merlangus merlangus	Lower Medway Estuary, U.K.	0.33	-	0.23-0.8	-	-	0.19-0.26	-	-	Wharfe and Van Den Broek, 1977
	Platichthys flesus	"	0.08-0.27	-	0.04-1.15	-	-	0.13-0.21	0.12	-	"
	Pleuronectes platessa	"	-	-	0.15-0.32	-	-	0.03-0.12	-	-	"
	Anguilla anguilla	"	0.32-2.06	-	0.16-0.87	-	-	-	-	-	"
	Liza macrolepis	Adyar Estuary	0.09	0.1	0.12	-	-	-	-	-	Nammalwar, 1985
	Pagothenia borchgrevinki	Antarctica	5-26.3	-	2.3-8.7	2.7-7.7	-	-	1.1-1.3	0.9-4.7	Honda *et al.*, 1983
Mn	*Mugil cephalus*	Kali Estuary	-	5.75	2.3	-	-	-	-	15.9	Veet *et al.*, 1992
	Silago sihama	"	-	7.7	0.4	-	-	-	-	11.69	"
	Leiognathus brevirostris	"	-	11.65	1.4	-	-	-	-	11.96	"
	Gerramorpha setifer	"	-	4.85	0.53	-	-	-	-	5.2	"
	Gadus morhua	Gdansk Bay	0.32	6.0	0.3	-	1.0	4.5-5.5	0.68	0.7	Szefer *et al.*, 1990
	Mya arenaria	"	-	10	260 (Mantle)	-	-	13	25	210	"
	6 Marine fishes	Aqaba, Jordan	ND-13.4	ND-26.8	ND-17.9	-	-	-	ND-13.4	-	Wahbeh and Mahasneh, 1987
	Pagothenia borchgrevinki	Antarctica	0.4-2.94	-	0.1-0.46	1.67-1.88	-	-	0.88-1.94	0.33-1.03	Honda *et al.*, 1983

TABLE 4 (Contd.)

Element	Species	Place	Liver	Gill	Muscle	Skin	Kidney	Intestine/ Gut	Gonad	Whole body	Source
Ni	*Gadus morhua*	Gdansk Bay	0.1	1.0	0.08	-	ND	0.04-0.1	0.1	0.1	Szefer *et al.*, 1990
	Mya arenaria	"	-	1.0	3.0 (Mantle)	-	-	0.5	0.25	1.4	"
	6 Marine fishes	Aqaba, Jordan	0.1-0.5	ND-0.3	0.1-0.6	-	-	-	ND-0.5	-	Wahbeh and Mahasneh, 1987
	Pagothenia borchgrevinki	Antarctica	0.04-0.66	-	0.02-0.23	0.12-0.13	-	-	0.06-0.14	0.05-0.12	Honda *et al.*, 1983
Pb	*Liza parsia*	Korapuzha Estuary	15.5	20.2	7.5	5.1	4.9	4.2	10.7	-	Mohapatra, 1993
	"	Cochin Backwater	0.9	5.1	0.1	1.3	2.4	0.7	0.8	-	"
	"	Tuticorin Bay	4.4	9.9	2.0	2.7	6.4	7.5	8.4	-	"
	"	Mandapam waters	11.7	8.0	2.6	5.3	5.7	3.7	19.3	-	"
	"	Ennore Creek	4.3	12.3	1.5	3.4	15.9	34.7	4.0	-	"
	"	Rusikulya Estuary	0.8	4.8	0.2	0.6	1.8	1.3	0.5	-	"
	Liza macrolepis	Adyar Estuary	1.51	2.83	1.25	-	-	-	-	-	Nammalwar, 1987
	"	Ennore Estuary	1.62	2.9	1.34	-	-	-	-	-	"
	Pleuronectes platessa	Lower Medway Estuary, U.K.	0.95-1.87	-	0.48-1.4	-	-	1.0-1.65	-	-	Wharfe and Van Den Broek, 1977
	Platichthys flesus	"	0.53-1.45	-	0.1-0.72	-	-	0.35-1.12	0.12	-	"
	Merlangus merlangus	"	0.25-1.54	-	0.18-0.46	-	-	0.2-0.67	-	-	"
	Pagothenia borchgrevinki	Antarctica	0.4-0.96	-	0.02-0.28	0.13	-	-	0.12-1.17	0.02-0.31	Honda *et al.*, 1983
	Gadus morhua	Gdansk Bay	0.4	4.0	0.2	-	ND	0.15-0.5	0.9	-	Szefer *et al.*, 1990

TABLE 4 (Contd.)

Element	Species	Place	Liver	Gill	Muscle	Skin	Kidney	Intestine/ Gut	Gonad	Whole body	Source
	Fishes	North Indian Ocean	3.8	3.14	1.11	-	8.61	-	1.36	-	Kureishy, 1985
	Anguilla anguilla	Lower Medway Estuary,	0.84-5.29	-	0.25-1.82	-	-	-	-	-	Wharfe and Van Den Broek, 1977
	6 Marine fishes	Aqaba, Jordan	ND-2.9	0.2-3.3	0.8-2.6	-	-	-	ND-2.6	-	Wahbeh and Mahasneh, 1987
Zn	*Liza parsia*	Korapuzha Estuary	51.7	54.5	15.3	79.9	33.7	71.1	223.8	-	Mohapatra, 1993
	"	Cochin Backwater	129.2	101.4	16.5	102.7	32.8	63.6	264.6	-	"
	"	Tuticorin Bay	185.9	60.4	34.5	9.13	66.5	91.7	211.4	-	"
	"	Mandapam waters	89.8	55.3	17.4	94.3	35.6	69.4	188.6	-	"
	"	Ennore Creek	150.9	121.4	15.6	64.7	55.3	73.1	333.3	-	"
	"	Rusikulya Estuary	19.8	53.6	14.1	56.4	77.9	100.2	355.5	-	"
	Mugil cephalus	North Atlantic	-	-	17.0	-	-	-	-	-	Windom *et al.*, 1973
	Liza macrolepis	Adyar Estuary	76.68	55.2	47.15	-	-	-	-	-	Nammalwar, 1987
	"	Ennore Estuary	86.65	45.2	67.3	-	-	-	-	-	"
	Morone saxatilis	-	35.9	-	3.8	-	-	-	-	-	Windom *et al.*, 1973
	Latridopsis ciliaris	-	90-1200	-	0.9-7.0	-	12.2	-	52-100	-	Brooks and Rumsey, 1974
	Gadus morhua	-	5.1-16.7	14.6	2.9-4.1	-	18.0	7-13	5.5-44.9	3.5	Szefer *et al.*, 1990
	Anguilla anguilla	Lower Medway Estuary, U.K.	40.4-95.8	-	13.9-36.4	-	-	-	-	-	Wharfe and Van Den Broek, 1977
	Merlangus merlangus	"	24.2-32.4	-	6.0-12	-	-	20.9-25	-	-	"
	Pleuronectes platessa	"	36.4-42.2	-	8.3-14.5	-	-	27.5	-	-	"
	Platichthys flesus	"	48.8-76	-	8.0-19.4	-	-	30.4-40.4	146.8	-	"

TABLE 4 (Contd.)

Element	Species	Place	Liver	Gill	Muscle	Skin	Kidney	Intestine/ Gut	Gonad	Whole body	Source
Zn	*Pagothenia borchgrevinki*	Antarctica	22.4-34.2	-	4.27-8.15	27.4-37.9	-	-	18.7-104	8.73-13.7	Honda *et al.*, 1983
	Mya arenaria	Gdansk Bay	-	31	23 (Mantle)	-	-	30	16	20	Szefer *et al.*, 1990
	6 Marine fishes	Aqaba, Jordan	31.1-720.3	69.4-145.6	7.0-58.9	-	-	-	150.4-417.7	-	Wahbeh and Mahasneh, 1987

mercury in axial muscle tissues, present mostly as methyl mercury (Phillips, 1977). It is reported that the total mercury content of the Atlantic bonito *Sarda sarda* increases with increasing size of the specimen (Capelli *et al.*, 1987). Organic mercury content also increases with the size of the specimen, whereas inorganic mercury remains constant. It is interesting to note that the mercury concentration in the gonads also increases with the size of the specimen. A very small difference between the total mercury content of white and dark muscle is observed. In *S. sarda* the Se, Zn, Cu and Mn concentrations are lower in white muscle than in dark muscle.

Chromium and nickel showed little evidence of concentrating preferentially in any organ, although Wright (1976) found slightly higher concentration of nickel in skin, liver and kidneys of teleosts than in other organs. According to Zingde *et al.* (1976) the liver and gills have more arsenic concentrating ability than the other organs. The accumulation of heavy metals in different tissues of marine and coastal organisms is given in Table 4.

8

BIOACCUMULATION FACTOR OF HEAVY METALS IN MARINE ORGANISMS

Bioaccumulation Factor or Bioconcentration Factor (KB) indicates how many times a fish concentrates a metal above a certain environmental level which is usually (but not always) that of water (Dallinger *et al.*, 1987). If the accumulation of metals in tissues is expressed in ppm dry wt., for the purpose of calculation the metal content in the tissues is to be back converted to wet weight basis with the help of moisture content value for each specific tissues (Mohapatra, 1993).

The calculation of the KB is done by the formula (Buikema *et al.*, 1982; Nair, 1984)

$$\text{KB} = \frac{\text{Concentration of an element in the tissue}}{\text{Concentration of the element in the water}}$$

As the unit of metal in tissue is in ppm and that of water in ppb, the units of the tissue were multiplied by 1000 before the calculation to equalise, and KB has no unit.

For *e.g.*

$$\text{Unit of KB} = \frac{\text{ppm}}{\text{ppb}} = \frac{\text{ppm x 1000 = ppb}}{\text{ppb}} = \text{No unit}$$

Indeed, of all marine organisms examined, algae together with oysters and scallops have the greatest ability to absorb heavy metals from its surrounding environment (Eisler, 1979). High biomagnification from sea water was the rule among the molluscs (Eisler, 1981). The bivalves from Greek water contained 4,100 to 15,000 times more copper than the ambient medium (Papadopoulu, 1973). Among molluscs, highest KB was generally

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TABLE 5. Bioaccumulation Factor of heavy metals in different tissues of marine organisms

Element	Species	Place	Liver	Gill	Muscle	Skin	Kidney	Intestine	Gonad	Whole body	Source
Cd	*Crassostrea* spp.	Goa estuarine waters	-	-	-	-	-	-	-	3,00,000	Zingde *et al.*, 1976
Cu	*Liza parsia*	Pooling for Korapuzha Estuary, Cochin Backwater, Tuticorin Bay, Mandapam waters, Ennore Creek, Rusikulya Estuary	2735	259	289	353	1306	519	428	-	Mohapatra, 1993
	Crassostrea cuculata and *C. gryphoides*	Goa estuarine waters	-	-	-	-	-	-	-	14,000	Zingde *et al.*, 1976
	Ascelis indicus	Bombay Harbour Bay	-	-	-	-	-	-	-	2,000	Matkar *et al.*, 1981
	Scylla serrata	"	-	-	-	-	-	-	-	4300-6200	"
	Arius sp.	"	-	-	-	-	-	-	-	160-790	"
	Penaeus indicus	Cochin Backwater	-	-	-	-	-	-	-	139-3049	Anikumari, 1992
	Pleuronectes platessa	Pacific	-	-	-	-	-	-	-	130-660	Vink, 1972
	Hippoglosus stenolepis	"	-	-	-	-	-	-	-	50-250	Waldichuk, 1974
Fe	*Arius* sp.	Bombay Harbour Bay	-	-	-	-	-	-	-	310-1200	Matkar *et al.*, 1981
	A. indicus	"	-	-	-	-	-	-	-	1500	"
	Scylla serrata	"	-	-	-	-	-	-	-	600-1200	"
Hg	*Mystus gulio*	Ennore Estuary	-	-	-	-	-	-	-	3	Joseph and Srivastava, 1993
Mn	*Arius* sp.	Bombay Harbour Bay	-	-	-	-	-	-	-	510-1300	Matkar *et al.*, 1981
	Scylla serrata	"	-	-	-	-	-	-	-	1700	"
Pb	*Liza parsia*	Pooling for Korapuzha Estuary, Cochin Backwater, Tuticorin Bay, Mandapam waters, Ennore Creek, Rusikulya Estuary	964	439	86	234	642	164	1087	-	Mohapatra, 1993

TABLE 5 (Contd.)

Element	Species	Place	Liver	Gill	Muscle	Skin	Kidney	Intestine	Gonad	Whole body	Source
	Crustaceans	-	-	-	-	-	-	-	-	100	Heyraud and Cherry, 1979
	Sergestes spp.	-	10-1,00,000 (Hepato-pancreas)	-	-	-	-	-	-	"	
	Penaeus indicus	Cochin Backwater	-	-	-	-	-	-	-	upto 3476	Anikumari, 1992
	Hippoglosus stenolepis	Pacific	-	-	-	-	-	-	-	6000-10,000	Waldichuk, 1974
Trace metals	Bivalves	In general	-	-	-	-	-	-	-	10^3-10^6	Phillips, 1977
Zn	*Liza parsia*	Pooling for Korapuzha Estuary, Cochin Backwater, Tuticorin Bay, Mandapam waters, Ennore Creek, Rusikulya Estuary	1581	582	245	1392	862	1083	3421	-	Mohapatra, 1993
	Scallops	-	-	-	-	-	1.7-4.0 million times	-	-	-	Bryan, 1973
	Ostrea sinuata	-	-	-	-	-	-	-	-	1,00,000	Brooks and Rumsby, 1965
	Crassostrea virginica	-	-	-	-	-	-	-	-	1,00,000	Pringle *et al.*, 1968
	Surf clam	-	-	-	-	-	-	-	-	1,525	"
	Mercenaria mercenaria	-	-	-	-	-	-	-	-	2100	"
	Hippoglosus stenolepis	Pacific	-	-	-	-	-	-	-	1600-2100	Waldichuk, 1974
	Crassostrea spp.	Goa estuarine waters	-	-	-	-	-	-	-	1,00,000	Zingde *et al.*, 1976
	Arius sp.	Bombay Harbour Bay	-	-	-	-	-	-	-	650-2100	Matkar *et al.*, 1981
	A. indicus	"	-	-	-	-	-	-	-	770	"
	S. serrata	"	-	-	-	-	-	-	-	4200-5700	"

observed in cephalopods and oysters; in blood, digestive gland and kidney (Eisler, 1981). According to Senthilnathan *et al.* (1998) the maximum concentration factor was seen in oysters than mussels. In *L. parsia* the liver and kidney recorded higher Bioaccumulation Factor for copper; ovary for zinc and lead (Mohapatra, 1993). The ability of tuna to accumulate higher amount of lead from sea water is reported by Heyraud and Cherry (1979). Concentration factors for whole tuna were approximately 100, being highest in liver and lowest in muscle. The Bioaccumulation Factor of heavy metals in different tissues/ whole marine/estuarine organisms is given in Table 5.

9

MONITORING OF HEAVY METALS IN WATER

Biological and ecological techniques for monitoring effects of pollutants have developed rapidly. Many techniques are now available which approach chemical techniques in their sensitivity and which show pollution effects at sites hitherto not suspected of being polluted. Future developments of such techniques are likely to involve development of better water and sediment bioassay techniques. Molecular biological techniques already show promise of revolutionising approaches to effective monitoring. Finally, it is suggested that, it is not necessary to demand that a given biological technique must show an effect at a higher level of organisation than that at which it is tested (*i.e.* if induction of an enzyme in response to stress can be demonstrated, one does not need to show effects at population levels before regulatory action is taken). Some of the pollution monitoring techniques are discussed here.

9.1 Biomarkers of stress

One group of biological tools that are useful for monitoring exposure to xenobiotics (and hence water quality) have been collectively referred to as biomarkers. Biomarkers within an aquatic toxicological context generally represent biological responses of individual organisms to xenobiotic exposure (*i.e.* responses at the whole organism level of biological organisation). These include among others, enzyme alterations, bile metabolites, RNA/DNA ratio, adenylate energy charge, skeletal abnormalities, immune dysfunction, behavioural changes and histopathological lesions. Biomarkers can act as effective early warning sentinels to ensure the protection of the integrity of whole ecosystems, including freshwater and marine ecosystems. The application of fish mixed function oxidase (MFO) and cytochrome P-450 as biomarkers of chemical exposure in Port Phillip Bay is reported by Holdway *et al.* (1995). Interest is growing in biological markers, "measurements of body fluids, cells, or tissues that indicate in biochemical or cellular terms the presence of contaminants or the magnitude of the host response". Rapid, sensitive and quantifiable, biochemicals and molecular alterations comprise biomarkers of exposure. However, relation to toxicity is often not understood. Chronic alterations, including xenotoxic responses, are more appropriately "biomarkers of adverse affect". However, with chronic duration, host cellular responses appear and these sequelae lesions often obscure the prior toxicant-induced changes. Infectious disease may be an indication of prior toxicant-mediated immunosuppression or conversely the expression of only one of multiple stressors on which toxicant-induced injury may be superimposed. Correct interpretation of lesions and biomarkers in feral fishes requires basic scientific integration of infectious disease and toxicity.

In a field study DNA damage, haematological parameters and liver somatic index (LSI) were measured in fish collected from freshwater creeks of East Tennessee contaminated with polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) and from estuarine and marine waters of Mississippi Sound contaminated with PAHs and cadmium (Everaarts *et al.*, 1993). For comparison, specimens were examined from two pristine reference sites near the impacted Tennessee and Mississippi sites. Significantly more strand breaks were found in DNA isolated from liver tissue of redbreast sunfish *Lepomis auritus* from contaminated creeks than two pristine creeks. Haemoglobin concentration C_{Hb} and mean corpuscular haemoglobin concentration (MCHC) were significantly higher in both male and female sunfish from the pristine creeks. Further more, the liver somatic index of sunfish from contaminated creeks was higher than that of specimens from reference sites. In adult male, female and juvenile hardhead catfish *Arius felis* from suspected contaminated sites in the Mississippi Sound, high LSI and lowered C_{Hb} and

MCHC were found. A higher percentage of double stranded DNA was measured in specimens from the pristine sites.

Hepatic monooxygenase activity can be induced by many different environmental chemical contaminants (Haasch *et al.*, 1993) and measurement of this activity has been proposed as an environmental biomonitor. The use of cytochrome P4501A (CyP1A) as a biomarker of organic pollution was investigated in liver of goby and digestive gland of mussel (Livingstone *et al.*, 1993). Elevated 7-ethoxyresorufin 0-deethylase (EROD) activity and CyP1A-protein levels in goby were correlated with high tissue contaminant levels at the industrial site of Porto Marghera. Indications were obtained of elevated levels of CyP1A-like mRNA, CyP1A-like protein and microsomal metabolism of benzo(a)pyrene to free metabolites in mussels from the industrial CVE site in Venice compared to a site in the Adriatic Sea. The above studies demonstrated the usefulness of CyP1A as a biomarker for organic pollution in fish and indicate some potential for its application in molluscs.

A variety of environmental stressors have been shown to induce alterations in gene expression. This response appears to be universal between species. The changes in gene expression in hepatocytes of channel catfish *Ictalurus punctatus* exposed to Pb was reported by Glaven *et al.* (1993). Induction of stress protein in hepatocytes was examined after acute exposures. Most striking was the detection of an apparent new protein of molecular weight 50-55 kDa in response to Pb. The induction patterns of this protein occurred in a dose response manner. The synthesis of a 30-32 kDa protein was increased with exposure of Pb. The increased synthesis of a protein in the 25-kDa range was also detected at low and medium doses of Pb. Such data raises the possibility of monitoring early changes in cellular responses to Pb in fish *via* induction of specific stress protein response patterns at low dose levels and early time points. Thus these biochemical fingerprints may be useful as biomarkers of sublethal chemical exposure in the aquatic environment.

9.2 *Mussel watch*

Mussel watch, one of the operation contaminant monitoring approaches based on the sentinel organism concept used as a global scale monitoring programme that is capable of detecting trends in concentrations of some marine contaminants. The bivalve molluscs accumulate heavy metals in their tissues. Species of *Mytilus* and *Crassostrea* have been used with considerable success for monitoring programmes. If mussels and oysters grow at the same location, it is observed that oysters are more effective bioaccumulators for Zn, Cu and Cd (Krishnakumar *et al.*, 1990) and mussels for Pb and Mn. The green mussel *Perna viridis* has been proposed as a biomonitor of trace metal in tropical waters (Phillips, 1985).

According to Krishnakumar *et al.* (1990) kidney and mantle of *P. viridis* showed significant differences for bioaccumulation of trace metals. Mussel shell was found to be showing higher concentrations of Cu, Pb and Mn compared to the soft tissues. But, the differences between the shell metal concentrations from the clean and polluted sites were found to be not significant. Foot and posterior adductor muscle were found to be poor reflectors of trace metals in the environment. It is reported that digestive and basophil cells of digestive gland and nephrocytes of kidney are involved in the metabolism of wide range of metals and the elemental composition of deposits inside these cells reflects the presence and availability of environmental pollutants (Mason *et al.*, 1984). It is therefore useful, in monitoring programme to select a specific tissue which shows maximum proportional response to changes in the environment rather than analyse the whole organism (Mason and Simkiss, 1983).

According to Krishnakumar *et al.* (1990) kidney is the major site of accumulation of Zn and Cd in *P. viridis*. Similar results are reported in *Mytilus edulis* (George, 1983; Lobel, 1987). George (1983) has reported that more of the zinc and cadmium in the mussels are stored in the kidney in membrane bound granules.

Bivalves obtain metals through the food and by direct uptake from the seawater. The intracellular digestion and absorption of the food takes place in the digestive cells of the digestive gland, thus, attributing high concentration of metals in the digestive gland.

Metallothionein induction in response to chemical stressors in mussels (Viarengo *et al.*, 1988; Hogstrand and Haux, 1990) has been shown to be a reliable technique which indicates that heavy metals are a problem if metallothionein induction is measured. Another technique which has been shown to be consistently reliable as an indicator of general stress is scope for growth in mussels (Bayne, 1980; Widdows and Johnson, 1988). Scope for growth is reduced in response to increased body burdens of polyaromatic hydrocarbons and PCBs (Widdows and Johnson, 1988). Hawkins *et al.* (1986) have shown that the mussel protein turnover is genotype dependent and therefore a genetically determined contributor to variability between individuals in growth rate. Koehn and Baryne (1989) argue that stress acts differentially on individuals according to the efficiency with which they meet their metabolic requirements. Thus, the technique has reached a stage that it can be routinely applied, but basic research continues to establish the physiological and genetic basis of the measured response.

9.3 Cytochrome P450 system in fish

Another technique which has been proven to be reliable and applicable in monitoring programmes is induction of enzyme systems in response to given stressors. The cytochrome P450 system in fish has been refined and applied to a number of different gradients and shown to be reproducible (Addison and Edwards, 1985; Stegeman *et al.*, 1990).

From a number of studies carried out (Payne *et al.*, 1987; Haux and Forlin, 1988) it has become clear that the P450 1A1 mediated monooxygenase activities (EROD and AHH) often are elevated in fish from polluted waters. In the work of Payne and Penrose (1975) increased hepatic AHH activity was observed for the first time in brown trout taken from a small urban lake in Newfoundland with a history of hydrocarbon contamination. Subsequent studies have shown that fish caught in waters contaminated with oil hydrocarbons, industrial or municipal wastes exhibit increased P-450 monooxygenase activity. The interpretation of most of these field studies requires a reference station located in an unpolluted area with fish of similar age and sex. In addition the interpretation in most cases relies upon the fact that the response is relatively specific with respect to the inducing chemical.

9.4 *Metallothioneins*

Metallothioneins (MTs) are low molecular mass, cystine-rich metal binding polypeptides. MTs were first reported for an aquatic species by Olafson and Thompson (1974) who described the existence of low molecular weight, cadmium binding proteins in the marine fish *Sebastes seboides.* This was soon followed by reports of metallothionein in other fish species and the marine molluscs *Crassostrea virginica* (Casterline and Yip, 1975) and *Mytilus edulis* (Noel-Lambot, 1976). The widespread occurrence of MTs in aquatic species is now firmly documented (Roesijadi and Fowler, 1992).

The use of MTs in monitoring the effects of metals have also been made for aquatic organisms in contaminated environments (Bayne *et al.*, 1988). The potential use of MT as a specific biochemical probe for metal exposure of aquatic organisms was recognised early (Brown *et al.*, 1977). Considerable progress has been made on the structure and behaviour of MTs in aquatic organisms although an understanding of the specific intracellular function of MT and the biological and environmental factors that influence such function is still limited. Thus, it has been advised that use of MTs in applied monitoring efforts proceeds with caution.

With current methodologies, MT induction can be measured at several levels *i.e.* increase in metal content in the MT pool, increase in MT and increase in MT mRNA. Each reflects a different level of cellular regulation and function and provides complementary information.

9.5 DNA damage

In aquatic systems, the evaluation of DNA damage in various organs of fish and in tissue samples of molluscs indicates the level of pollution in environment. A large variety of environmental carcinogens are metabolically activated to electrophilic metabolites that can bind to nucleic acids forming covalent adducts. In organisms possessing active metabolic systems for a particular carcinogen, DNA adduct generally have longer biological half-lives than the substrate carcinogens. Thus, measurement of specific DNA adduct concentrations in terrestrial and aquatic organism may provide a relevant biological indicator of prior exposure to environmental carcinogens (Van-Schooten *et al.*, 1995). According to Ericson *et al.* (1995) *Perca fluviatilis* were sampled from unpolluted and polluted areas in Swedish coastal waters. The level of aromatic/hydrophobic DNA adducts in liver tissue was analysed using the nuclease P1 version of the ^{32}P-post-labelling assay. The level of total adducts measured in the individual fish from polluted areas was between 6 and 22 nmol of adducts/mol of nucleotides, and in the fish from the reference area between 0.2 and 0.6 nmol of adducts/mol of nucleotides.

At the community level while the multivariate techniques have been shown to detect subtle changes in biological systems along contaminant gradients the results are still correlative rather than indicating cause and effect. Thus, research in the application of these techniques to pollution monitoring is concentrating on ways to link biological and chemical data so that cause-effect relationship can be established. This linkage between chemistry and biology is one that must run through the application of all biological effects techniques. Chemical and biological sampling must be done together so that proper linkages and better cause-effect relationships are established so that we move away from detection effects to their prediction.

10

CONTROL OF HEAVY METAL POLLUTION

To arrive at acceptable concentration of metals in the effluents from industrial premises, the concentrations already present in the receiving stream or system must be determined, and the quantity which would bring these concentrations upto the acceptable limits, calculated.

10.1 Treatment of metal finishing effluents (Conventional chemical treatment)

The cyanides and chromates must be destroyed; cyanides normally by chlorination under alkaline conditions and chromates by reduction with sulphur dioxide or sulphites under acid conditions. After this, the effluents can be brought to an acceptable pH level, normally between 6 and 10, but sometimes between 7 and 9, at which level they are acceptable for discharge to both sewers and rivers/coastal waters. At these pH values all the toxic or undesirable metallic radicals in solution, such as Cu, Zn, Cd, Ni, Fe and Cr are precipitated as insoluble hydroxides and so can be removed by settling out or filtration (Baier, 1974).

10.2 Sewage treatment for heavy metals

In the process of purification, the damage to purification plant depends on the level of concentration of the metals present in the sewage. When the total concentration of Pb, Cu, Zn, Cd, Cr and Ni is less than 10 mg/l, it is possible that some of the metals are essential for the proper functioning of biological processes (Dickinson, 1974 b). In the circumstances where sewage treatment is restricted to physical methods only, the affinity of metals for organic matter is an advantage since their concentration in solution is considerably reduced as a result, without any harm to the treatment plant. The approximate extent to which sewage purification plant will remove these metals when their concentration do not exceed 10 mg/l in the sewage. Otherwise, the plant can not remove the metals effectively (Jenkins *et al.*, 1964).

Removeal of heavy metals by sewage treatment : 10 ppm level		
Metal	Sedimentation only %	Sedimentation followed by biological purification (%)
Pb	50	90
Cu	40	80
Zn	60	80
Cr	25	50
Ni	30	30

The solubilities of metals in sewage depend on many factors, such as the pH value, the temperature and the time of contact. When combined with organic matter, the metals become insoluble and are deposited in sedimentation tank or in the bed of stream or river or basin.

10.3 Water purification by ion exchange

In fact, effluent treatment by ion exchange is merely a method of concentrating and partially separating the contaminating radicals so that they can be precipitated out more easily by classical chemical methods. The principle is that the effluents are passed first through a bed of cation exchange resin where contaminating metal ions are exchanged for hydrogen ions from the resin.

In practice 99% of all ion exchange resins produced in the world are used in water treatment, or closely allied application (Arden, 1968). Its purpose is to make water colourless, clear, free from odour and bacteriologically sterile.

Many different types of chemical compounds can be used to form ion exchange materials. Indeed, the most common ion exchange material in the world is ordinary clay soil in which the crystalline alumino-silicate structure gives the locked anion, while cations can freely replace each other in the crystal network. For *e.g.* if ammonium sulphate is passed through a tube of soil, the ammonium is absorbed and calcium sulphate solution emerged from the calcium.

10.4 Recovery of water and by-products from industrial wastes

The metal finishing industry is a prolific consumer of water, used chiefly for washing metal parts after the various stages of pickling, electroplating or anodizing. It is then normally discharged to sewer or even to river and toxic constituents such as cyanide or chrome must be removed before discharge. The water must be purified through classical methods of precipitation, thickening and filtration. Any fault in operation results in the illegal discharge of toxic materials to drain. The demineralisation of the effluent liquor with circulation of the pure water for reuse removes the main effluent disposal problem. The equipment is controlled by the standard method of conductivity measurement. Regeneration of the resins produces small volumes of relatively concentrated solutions of toxic metals on the one hand and obnoxious anions such as chromate and cyanide on the other. These solutions are then treated batchwise in small scale equipment, the treated liquors being stored until laboratory checks have proved them to be a suitable standard for discharge.

10.5 Waste liquid treatment

The design of the treatment system depends on the waste composition, the permissible discharge levels, and the amenabilities of the pollutants to treatment by the multitude of available methods. The common treatment processes for dilute waste water include : equalisation, neutralisation, clarification, biological oxidation and recovery of specific compounds (Ross, 1968).

The effluent discharge in estuaries or coastal waters must not have deleterious effects on fish and fishing. Whenever an effluent discharge can be made in such a way that, with large volumes of water available for dilution, a quick dispersion of the harmful compounds is practicable. There is less need to take special steps to ensure that all harmful products are reduced to minimum before the effluent is discharged. A special problem arising in tidal rivers, however, is that of accumulation of effluent within the mouth of the estuary due to the piston action of rising and falling tides, and the relatively small flow seaward of freshwater compared with the vast volumes of sea water concerned in the tidal rise and fall. To overcome these difficulties of discharge in estuaries, recourse is sometimes made to the provision of "holding tanks" or other means whereby effluent discharges are made only for some two or three hours after high water, to enable adequate dilution to take place before the change of tide causes water to flow back up the river.

Discharge to sea although at first sight straight forward, is only satisfactory if adequate consideration is given to the best location for the final outfall, having regard to coastal currents, prevailing winds and the line of low water at minimum spring tide. In some instances, with particularly difficult effluents, it has been found necessary to arrange for disposal by conveying to deep water by barge. This is generally an expensive undertaking and is limited to those effluents for which there seems to be no other satisfactory solution (Hewson, 1963).

10.6 Heavy metals removal from water - A review

Metals	Methods of removal
Ba	By precipitation as barium sulphate by addition of sodium sulphate. Barium sulphate is insoluble. Coagulation of suspended solids in the waste water (including the finer non-settleable barium sulphate particles) with ferric sulphate provided solid removal. Through ion exchange.

Metals	Methods of removal
Cd	Precipitation : Cadmium forms an insoluble and highly stable hydroxide at alkaline pH. In the presence of complexing agents (*e.g.* cyanide), it is impossible to precipitate out the cadmium ion. By application of lime increase the pH to 9.0 and above for precipitation to occur. Ion exchange, Evaporative recovery.
Cr	Precipitation, ion exchange, evaporative recovery. The standard reduction treatment technique is to lower the waste stream pH to 3.0 or below with H_2SO_4 and convert the hexavalent chromium to trivalent chromium with a chemical reducing agent such as sulphur dioxide, sodium bisulphite or ferrous sulphate. The trivalent Cr is then removed usually by precipitation with lime or caustic soda. Sulphur dioxide appears to be the most popular reducing agent. Chemical precipitation involves chemically removing Cr ions from industrial waste solutions by direct precipitation with barium carbonate in such solutions acidified with nitric acid or hydrochloric acid or their salts.
Cu	Precipitation, ion exchange, evaporation, electrolysis, filtration. Precipitation of insoluble metal hydroxide at alkaline pH (by addition of lime). The standard domestic sewage tertiary treatment sequence is chemical coagulation, sedimentation and sand filtration. The effluent from a settling tank is passed through a relatively thick filter bed of a suitable filter material such as dolomite. When the filter bed becomes clogged, it is backwashed to remove the copper contaminants therefrom and the backwash water and the copper contaminants are returned to the settling tank for resettling.

Metals	Methods of removal
Fe	The primary removal process for iron is conversion of ferrous iron to the ferric state and precipitation of ferric hydroxide near pH 7 where its solubility is at a minimum. Lime is used for pH adjustment. McCracken (1961) reports that results of pilot plant operation where 9.0 mg/l iron was reduced to 0.5 mg/l with chlorination, lime addition and sand filtration. Soluble iron and manganese removal from water by treatment of the water with permanganate ion and filtration through a manganese oxide zeolite bed. Deep well injection through pressure.
Pb	Treatment of dissolved lead involves for the most part, reaction to form a lead precipitate and sedimentation. In the precipitate process lead is normally precipitated as the carbonate ($PbCO_3$) or the hydroxide ($Pb(OH_2)$). The solubilities of both compounds are very low at alkaline pH. In forming soluble lead hydroxide, lime is the treatment chemical of choice. The precipitation can also be assisted by addition of ferrous sulphate which acts as a flocculating agent. Precipitation of dissolved lead by dolomite ($CaCO_3$. $MgCO_3$) to yield lead carbonate has also been reported. Ion exchange.
Mn	Conversion of soluble manganous ion to an insoluble precipitant. Lime soda type treatment gives removal at pH 9.5. Add permanganate and filter through sand filter. Chlorination followed by lime coagulation and rapid sand filtration. Ion exchange.
Hg	A process developed by Knepper (1972) is one in which mercury recovered from waste waters is accomplished by converting the mercury to low-water-solubility compounds and/or to metallic mercury by the use of

Metals	Methods of removal
	precipitants and subsequent separation thereof from the waste water. The mercury is probably converted to mercuric sulphide by precipitation with the preferred compound hydrogen sulphide or other compounds which yield sulphide ions. The mercury can also be converted to metallic form by reduction with reducing agents such as non-noble metals and low molecular aldehydes. The precipitant is used in chemical equivalent amounts directly proportional to the dissolved mercury content of the waste water, and it is advisable to add an excess amount of precipitants upto 10^{-4} - molar and preferably upto 100 molar. After addition of the precipitant, a holding period of atleast 5 seconds, preferably 15 to 500 seconds and especially 30 to 120 seconds is required to permit the precipitation to take place before separation of the formed low-water - solubility mercury compounds and/or metallic mercury. Convention means such as settling tanks, filter and the like can be used for separating the precipitated mercury compounds and/or metallic mercury from the waste water.
Ni	Formation and precipitation of nickel hydroxide is the basis of destructive treatment of nickel bearing wastes. It is done by addition of lime. The precipitation is most effective at high pH. The use of lime followed by ferric chloride (to improve de-watering) and sand filtration is an effective method and can reduce nickel to 1.0 mg/l. Ion exhcange. Evaporative recovery from the rinse water of the plating bath.

Metals	Methods of removal
Se	Lime coagulation and settling (16.2%), cation plus anion exchange (99.7%) by strong acid - weak base ion exchange system.
Ag	Precipitation as silver chloride which is insoluble in water under acidic condition. Ion exchange.
Zn	Chemical precipitation at alkaline pH. Zinc removed as zinc hydroxide. Lime is used for pH adjustment. Precipitation followed by flocculation and sedimentation. With lime treatment levels below 1 mg/l of zinc are readily obtainable. Removal of precipitated zinc from the effluent system may require sand filtration. Ion exchange recovery seems feasible only for large scale operation and with high zinc concentration in the waste waters.

The studies on aquatic plants living in various bodies of water and effluent from mines and also in laboratory experiments have revealed the accumulation of heavy metals to a marked extent (McLean and Jones, 1975; Welsh and Denny, 1980; Mishra *et al.*, 1991; Mohapatra and Rengarajan, 1996). The use of bryophytes for monitoring metal pollution has also been reported and discussed (Say *et al.*, 1981; Wolverton, 1981; Whitton *et al.*, 1982; Wehr and Whitton, 1983).

11

CONCLUSION

Heavy metals in the wrong place at the wrong time and in the wrong concentration can be extremely noxious. But, metals are an integral component of the environment and of living matter. Some have a beneficial biological influence when present in certain concentrations. Others have no evident positive biological effect and their only known impacts are harmful. However, toxic effects are possible with any metal whenever its dose exceeds a critical level.

Aquatic ecosystems are not usually able to eliminate heavy metals from waste discharges by their own natural processes. Mercury, cadmium, arsenic and copper tend to accumulate in bottom sediments, from which they may be released by various processes of remobilisation. They can then in different form move up through biological food chains, eventually to humans.

This book reviewed different types of heavy metals available in estuarire, marine and coastal ecosystems, their source, impact on organisms, bioaccumulation and their possible control in the waste waters before releasing the same to the natural water bodies.

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GLOSSARY

(Brief definition/explanation/expansion of some important terms used in this book. For more terms, please refer CMFRI Special Publication No. 64 (1995) by the same authors)

Absorption : Penetration of one substance into the body of another.

Accumulation : To go on increasing; the action or process of accumulating.

Acid : It is regarded as a substance which accepts electron or gives H^+ ions in solution.

Acidity : The quantitative capacity of aqueous media to react with OH^- ions or to accept electrons.

Adsorption : Taking up of one substance at the surface of another.

Alkali : It is regarded as a substance which donates electrons or gives OH^- ions.

Alkalinity : The quantitative capacity of aqueous media to react with H^+ ions or to donate electrons.

Alkalinity total : The total alkalinity of water is mainly caused by the cations of Ca, Mg, Na, K, NH_4 and Fe combined either as carbonates and/or bicarbonates or occasionally as hydroxides.

Algicide : Any substance which is toxic to algae.

Backwater : Part of a river not reached by its current, where the water does not flow (Hornby and Cowie, 1984).

Base : It is regarded as a molecule or ion which can accept a proton given off by an acid in solution.

Bay : Part of the sea or of a large lake, enclosed by a wide curve of the shore (Hornby and Cowie, 1984).

Bioaccumulation : Uptake and retention of environmental substances by an organism from its environment, as opposed to uptake from its food.

Biomagnification : Passing of a substance through food chain such that each organism retains all or portion of the amount in its food and eventually acquires a higher concentration in its flesh than in the food.

Bioremediation : The use of micro-organisms to breakdown pollutants and waste in soil and water to harmless or less toxic end products which may be either simple inorganic chemicals such as water and CO_2 or less toxic components of the starting material.

Bivalve : An animal with a hinged two-valve shells examples are the clam and oyster.

Buffer : The mixture of a weak acid and salt of it with a strong base or a weak base and salt of it with a strong acid is called buffer. The pH remains constant in a solutioin if buffer is added in it (when temperature remains constant).

Chelating agent : The chemical compounds which have the property of withdrawing ions from solution to form closed ring soluble complexes.

Chlorination : The use of chlorine to water, industrial waste, or sewage for disinfection and other biological or chemical results.

Coagulation : A water treatment process in which chemicals are added to combine with or trap suspended and colloidal particles to form rapidly settling aggregates.

Coast : Land bordering the sea; sea shore and land near it (Hornby and Cowie, 1984).

C.O.D. (Chemical Oxygen Demand) : The amount of oxygen (mg/l) consumed under specified conditions in the oxidation of organic and oxidisable inorganic matter contained in industrial waste water, corrected for the influence of chlorides.

Colloids : The finely divided solid particles of diameter varying from 10^{-5} to 10^{-7}cm. They can not be filtered through ordinary filter paper.

Corrosion : The chemical action by which metal is converted into a compound and thus deteriorated.

Creek : Narrow inlet of water on the sea-shore or in a river bank (Hornby and Cowie, 1984).

Crustacea : Mostly aquatic animals with rigid outer coverings, joined appendages and gills. Examples are crayfish, crab, prawn, etc.

Dilution : An operation of disposing of sewage, industrial waste or sewage treatment plant effluent by discharging it into a stream or body of water.

Dilution Factor : $\dfrac{\text{Quantity of untreated sewage x 100}}{\text{Average quantity of diluting water available at the point of disposal}}$

Estuary : The ecotone or buffer zone between freshwater of the stream and salt water of the sea is called estuary. An estuary is a semienclosed coastal body of water which has a free connection with the open sea and within which sea water is measurably diluted with freshwater derived from land drainage.

Flocculation : A process of chemical, mechanical or both, by which small particles of solids in liquid are aggregated into larger masses, thus making easier for removal of solids by sedimentation.

Gulf : Part of the sea almost surrounded by the land (Hornby and Cowie, 1984).

Hardness : The water which contains bicarbonates, chlorides and sulphates of calcium and magnesium. It prevents production of abundant lather with soap.

Hardness total : The sum of carbonate hardness and non-carbonate hardness. Total hardness is the total of soluble calcium and magnesium salts present in the water, expressed as its $CaCO_3$ equivalent. Total hardness also includes the sulphates and chlorides of calcium and magnesium (Jhingran, 1991).

Index pollution : The measurement of degree of pollution in a stream as indicated by plankton, bacterial count, BOD or quantity of dissolved oxygen.

Mariculture : The term mariculture has come to mean organised culture of marine organisms in sea water.

Median Tolerance Limit (TLm) : The concentration of test material in a suitable diluent (experimental water) at which just 50% of test animals are able to survive for a specified period of exposure. It is ≅ LC50.

Mollusc (Mollusca) : A large animal group including those form popularly called shellfish (but not including crustaceans). All have a soft unsegmented body protected in most instances by a calcareous shell. Examples are mussels, clams, oyster, etc.

Monsoon : Seasonal wind blowing in the Indian Ocean from SW from April to October and from NE during the other months; the rainy season that comes with the wet (Hornby and Cowie, 1984). Months for SW monsoon are June to September (Qasim and Gopinathan, 1969) and for NE monsoon October to January (Lyla, 1991).

Organic matter : Organic matter present in natural water in solution is organic phosphorus, organic nitrogen, carbohydrates, vitamins, etc. That present in suspended states comprises the seston (Jhingran, 1991).

Parts per million (ppm) : A part per million is equivalent to a milligram of solute per kilogram of solution. Generally a part per million is considered equivalent to a milligram per litre, but this is not true.

Particulate matter : The matter in non-liquid state (not gas), which is dispersed in water to give a heterogenous mixture.

pH : The negative of the logarithm of hydrogen ion concentration in aqueous solution; low pH is acid, high pH is alkaline, pH 7 is neutral. $pH = \log [1/(H^+)]$.

Pollution : Any change is physical, chemical or biological properties of water or discharge of any sewage or industrial waste which may be harmful to public health or safety or animal life or to domestic, commercial, industrial, agricultural or other legitimate uses.

Pollution load : An expression of the quantity of pollutants present in a waste water discharged into a receiving water. It is expressed on the basis of BOD.

Polluted water : The water which contains industrial waste, sewage or other harmful or objectionable substances.

Pre-monsoon : Before the onset of monsoon. Months February to May for SW monsoon (Qasim and Gopinathan, 1969) and June to September for NE monsoon (Lyla, 1991).

Post-monsoon : After the monsoon. Months October to January for SW monsoon and February to May for NE monsoon.

Salinity : Salinity is defined as the total amount of solids in one kg of sea water when carbonates are converted into oxides, bromine and iodine are replaced by chlorine and all organic matter is completely oxidised.

Sedimentation : The setting of solid particles in a liquid system due to gravitation.

Shellfish : A group of molluscs and crustaceans usually enclosed in self-secreted shell; includes prawns, oysters and clams.

Sludge : A water formed sedimentary deposit generally in a very wet condition. It consists of suspended solid carried by water.

Sublethal : Involving a stimulus below the level that causes death.

Trace elements : There are certain elements called "trace elements" or "minor elements" which, even though occurring in extremely small amounts are of great significance in imparting productivity to waters.

Turbidity : Reduction of transparency of a sample due to presence of particulate matter. The turbidity of natural waters may be either due to suspended inorganic substances such as silt and caly, or due to planktonic organisms.

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