CHAPTER 1

REVIEW

The study of heavy metal pollution gained importance over the globe back. However, in India, it gained momentum quite recently. World Health Organisation has recommended measures on war footing to bring down the threat of heavy metal pollution. According to its estimate about 80 percent of water pollution in developing countries is caused by domestic wastes and the rest by industrial effluents [1].

Industrial, agricultural and domestic wastes pollute water with various heavy metals which reach human tissues through food chain [2]. Some of these heavy metals are essential which when present within admissible limits promote growth, normal metabolism and reproduction while some are toxic [3,4]. Therefore, it is essential to ensure the absence of toxic metals, and the presence of essential metals within permissible limit.

Heavy metals concentration in water, sediment and aquatic biota have been studied in New England River in U.S.A. [5] and rivers in East Tennessee [6]. Fytianos [7] studied the concentration of heavy metals in the lakes and rivers in Greece. Memmert [8] ascertained the seasonal fluctuations of heavy metal concentration in water and Daphnia obtusa. Saad et al. [9] reported the occurrence of certain heavy metals like Zn, Cu, Fe, Mn and Cd in lake Mariut in Egypt and their accumulation in various parts of Tilapia mossambica. Lopez and Lee [10] investigated the concentration of Cu in water in Torch Lake in Michigan and found the values as high as 0.117 mg/l and reported that it did not affect the fish and algal population. Bendell-Young and Harvey [11] determined the concentration of Mn in liver, kidney, muscle and bone of the White Sucker (Catostomus commersoni) from seven lakes in
South Central Ontario and its order of accumulation was bone > liver > kidney > muscle.


The concentration of heavy metals accumulation in marine organism from Aguada Bay in Goa was investigated by Singbal et al [16] who reported that the concentration of Mn, Fe, Cu, Zn and Hg ranged from N.D to 3.82, N.D to 22.17, N.D to 2.18, 3.20 to 22.66 and 0.12 to 0.41 mg/kg respectively. Hg concentration in seafood from the Arabian Sea, the Indian Ocean and the Bay of Bengal were reported to be within permissible limit [17,18,19]. Patel et al [20] found that in liver of *Anadara granosa* from Trombay, the Fe concentration was highest.

In the present investigation, an attempt has been made to study the concentration of heavy metals in water, sediment and fish from three different courses of water namely the Cauvery River, the Cooum Rivulet, and the Chetpet Pond in Tamilnadu situated in the southern part of India.

1.1 REVIEW OF INDIVIDUAL METALS

1.1.1 Mercury

Hg is an unique metal which exists in a liquid state at normal temperature and pressure. Of all the pollutants released into the environment, mercury is the most hazardous. Mercury forms both organic and inorganic compounds of which the organic form is toxic [21]. The organic form gets into fish and animals which in turn affects human beings who consume them. Drastic Hg poisoning has been reported in Iraq through bread made from treated wheat [22], in Mexico through pork reared
on treated grains [22] and in Minamata, Japan through polluted fish [23]. The major source of Hg is the natural degassing of the earth’s crust, quantities ranging between 25,000 and 1,50,000 tonnes of Hg per year being released. The Hg pollution in the environment is caused by waste disposal, chlor-alkali industry, paint industry, wood pulping industry, cement manufacture, smelting of metals, burning of fossil fuel, agrochemical industry, production of electrical equipments and medical instruments, dentistry and volcanic gases [24].

**Mercury in Water**

The concentration of Hg in drinking water is usually in the range of 0.000005 to 0.00001 mg/l, the average value being about 0.000025 mg/l. The forms of Hg in drinking water are not well studied but Hg$^{++}$ is probably the predominant species present as complexes and chelates with ligands [25]. In most surface waters, the levels are generally less than 0.001 mg/l [26,27,28]. In the polluted lakes and rivers in United States of America the levels were upto 0.03 mg/l [29]. In Indonesia, the levels in the river water ranged from 0.0023 to 0.027 mg/l while in sea water it was between 0.007 and 0.018 mg/l [30]. Raj [31] reported a high concentration of 0.001 - 0.0364 mg/l in the Cauvery River near Mettur, Tamilnadu, India where chlor-alkali industry is situated. Total Hg distribution in Ottawa River water was found to be approximately 0.00003 mg/l [32]. Imhoff et al. [33] evaluated the concentration of heavy metals in the Ruhr River between 1970 and 1978. The average concentration of Hg from the river mouth upto 127 Km decreased from 0.00007 to 0.00004 mg/l. Benedek and Laszlo [34] estimated mercury concentration in Danube waters over a period of three years from 1977 to 1979. The mean levels were 0.00032, 0.0008 and 0.00088 mg/l respectively for a mean flow discharge of 2350, 2110 and 2330 m$^3$/sec.

**Mercury in sediment**

Skei [35] reported a total Hg concentration of 350 mg/kg dry weight in sediments of Norwegian Bay. Although such levels were obtained in the immediate
vicinity of a chlor-alkali plant, collections made 2 km down from the effluent discharge yielded concentrations of 90-110 mg/kg dry weight only. Ramamoorthy and Kushner [36] found that the Hg concentration in Ottawa River samples below a paper mill was appreciably greater than that in samples above the paper mill during the period from 1972-1976. Kudo et al studied the movement of Hg from Minamata Bay into the Yatsushiro Sea. The study showed accelerated movement of Hg associated with Minamata Bay sediments during 1975-1978. The accelerated movement of Hg out of Minamata Bay during 1960-1975 was 9 metric tons, which increased to 17 metric tons during 1975-1978. The possibility of increased acceleration was attributed to commercial navigation in and out of the bay.

**Mercury in fish**

Fish and fish products contain Hg mainly in the form of methylmercury compounds to the extent of 70-90 percent of the total Hg content. The normal concentrations of Hg in edible tissues of various species of fish cover a wide range from 0.05 to 1.40 mg/kg fresh weight [38]. Total residues are usually higher in organs than muscle tissues. For instance the ratio of Hg concentration in liver to muscle in Black Marlin collected from Australia was 1.4:1 [39]. Raj [40] investigated the total Hg concentration in commercial fish species from the Stanley Reservoir (Mettur), India and reported them to vary from 0.135 to 0.220 mg/kg fresh weight. The residual Hg level in brain, liver and muscle of different types of fishes caught near a caustic-chlorine industry in Rushikulya River estuary, Orissa, India ranged from 0.34 - 1.89, 0.06-2.10 and 0.06-5.00 mg/kg fresh weight respectively [41]. Meranger and Smith [42] have reported that the average daily intake of Hg from food is, in the range of 0.010 to 0.012 mg but in regions where ambient waters have become contaminated with Hg and where fish comprises a high proportion of the diet, the intake from food may be much higher.
1.1.2. Copper

Cu is a very toxic, relatively accessible and essential heavy metal. Its presence in plant and animal tissue was recognized more than 150 years ago. It is a component metal in a number of enzymes [43]. Cu is an essential component of blood of gastropods and arthropods and is also necessary for the formation of haemoglobin in a range of animal species [3].

Copper in water

Cu and its compounds are ubiquitous and are thus frequently found in surface water. According to McKee and Wolf [44], the nature of Cu in water depends on the pH, carbonate concentration and other anions in solution. Cu levels in drinking water vary normally from 0.01 to 0.5 mg/l [45]. Montgomery and Santiago [46] reported that the total Cu concentration in the Guanajibo River mouth ranged from 0.0011-0.0024 mg/l. The average concentration of Cu in the Ruhr River ranged from 0.009-0.044 mg/l at a distance of 22 Km to 127 Km from the mouth of the river. Approximately 55 percent of the heavy metal load originated from the waste water and rest was of geochemical origin. About 31 percent of the total load was retained by sediment and subsoil [33]. According to Batley and Gardner [47], 40-60 percent of total Cu in estuarine and coastal waters was associated with colloidal matter of organic and inorganic forms. Koul et al [48] reported annual mean concentration of Cu in Khanpur, Trigam and Tilwan lakes to range from N.D to 0.1, 0.02 to 0.40 and N.D to 0.05 mg/l respectively.

Copper in sediment

Cu is sorbed readily to sediments and rate of sorption varies with the type of sediment, pH, competing cations and the presence of ligands and Fe/Mn oxides. In Lake Ontario, all the Cu in sediments was bound to humic acids [49]. In Amazon and Yukon Rivers only 8 to 15 percent of the total Cu was found to be organic [50]. However, Tessier et al [51] have reported a high percentage of organic bound Cu in
the particulates of Yamaska and St. Francois Rivers of Canada. The organic fractions from the two rivers were 31 and 51 per cent. The fractional distribution of the rest of the heavy metal was 42 and 22 percent for iron oxide, 20 and 12 percent for manganese oxide and 18 and 14 percent for carbonates between the two rivers respectively. Total Cu levels in fresh water sediments have been studied in Coeur d'Alene Lake, Natural Creek and Illinois River of U.S.A. and the average levels were 115, 102 and 19 mg/kg dry weights respectively [52,53,54]. Moore [55] reported an average of 350 mg/kg dry weight of Cu concentration at Yellow Knife Bay in Canada while comparatively a lower level of 39 mg/kg dry weight of Cu were found in Artic.

Copper in fish

Blevins and Pancorbo [6] reported Cu levels in fish to range from 0.08-0.87 and 0.07-0.81 mg/kg wet weight respectively in river and lake in East Tennessee, U.S.A. According to Powell et al [56] the Cu concentration in muscle of marine fish caught at Bougain-Ville Island in Papua New Guinea to range from 0.27-0.67 mg/kg fresh weight. Khan et al [19] have reported a Cu level of 0.65-58.1 mg/kg fresh weight in marine species caught from the Bay of Bengal.

Iron in water

Fe occurs in water mainly in the divalent and trivalent states [24]. Hart and Davies [57] have studied the concentration of Fe in the estuarine regions of the
Yarra River and reported that Fe is largely transported in colloidally bound forms. Salomons and Forstner [58] estimated the Fe concentration in the Mississippi River to be 0.055 mg/l. Similarly, a value of 0.012 to 0.130 mg/l was reported in the Danube River [59]. The mean value of 0.100 and 0.281 mg/l of Fe was reported in lakes and rivers of Greece [7] while the average of Fe in lake water in Egypt ranged from 0.0086 mg/l to 0.0399 mg/l [9]. Koul et al [48] studied the Fe concentration in lakes of Kashmir which ranged from 0.08 to 3.41 mg/l.

**Iron in sediment**

Grieve and Fletcher [60] have reported total Fe in suspended sediments from the Fraser River to range from 41000 to 48000 mg/kg dry weight. Fe concentration in sediments in Periyar River ranged from 11250 to 180000 mg/kg dry weight during post-monsoon season [13]. The Fe concentration in sediments in Danube River was between 2500 to 17000 mg/kg dry weight [34]. Jones and Jordan [61] reported that the Fe concentration in sediment was found to be 15000 to 132000 mg/kg dry weight in the upper reaches of the Liffey estuary, Dublin.

**Iron in fish**

Fe was estimated and found to be 38.39 mg/kg dry weight in marine fish from the Bay of Bengal [19]. Bowen [62] reported a maximum of 400 mg/kg dry weight of Fe in marine organisms while 2.96 to 22.17 mg/kg fresh weight was reported in Aguada Bay, Goa by Singbal et al [16]. The moderate Fe levels except for some higher values in fishes show the adaptive tendency of aquatic organisms in excreting the excess Fe consumed [43].

1.1.4 Manganese

Mn is the second most abundant metal of those. Biologically it is an essential micronutrient for most organisms. At optimum level it is beneficial while toxic at higher level both to animals and human beings. It is widely distributed in
nature in the form of compounds such as oxide, sulphide, carbonate and silicate. It can also occur in most iron ores in concentrations ranging from 50000-350000 mg/kg and in many other minerals [63]. A rough estimate of the average concentration of Mn in earth's crust is about 1000 mg/kg [64]. Mn usually accumulates in the subsoil and not on the surface, 60-90 percent of the Mn being found in the sand fraction of the soil [65]. In Indian soils, the total Mn content ranged from 37 to 11500 mg/kg [66].

**Manganese in water**

The Mn content of large rivers in the U.S.A. ranged from N.D. to 0.185 mg/l [67,68]. Abdullah and Royle [69] reported a range of 0.0008 to 0.028 mg/l of Mn in Welsh Rivers and lakes in Wales. Mn concentrations in the Rhine and the Maas and their tributaries ranged from 0.001 to 0.530 mg/l [70]. Slowey and Hood [71] determined total Mn concentration in the gulf of Mexico (0.0039 mg/l) which was greater than in the open sea (0.00031 mg/l). Reddy and Venkateswarlu [72] reported that Mn content of water ranged from N.D to 0.08 mg/l in the river Thungabadra and paper mill effluent channel. According to Kleinkopf [73] surface waters of various American lakes were found to contain a minimum of 0.00002 and a maximum of 0.0875 mg/l with a mean value of 0.0038 mg/l. Lopez and Lee [10] reported that Mn concentration ranged from 0.008 to 0.132 mg/l in unfiltered water in Torch Lake, Michigan (U.S.A). Koul et al. [48] reported that the Mn content in Khanpur, Trigam and Tilwan Lakes in Kashmir ranged from 0.010 to 0.460, 0.011-0.450 and 0.165-0.750 mg/l with an average of 0.195, 0.272 and 0.424 mg/l respectively. They concluded that these waters were unfit for human consumption.

**Manganese in sediment**

Mn content of stream sediments from Welsh Moorlands with rock and soil was 540 and 300 mg/kg dry weight respectively [64]. According to Cronan [74] Mn content in Pacific Pelagic clay ranged from 3670 to 10260 mg/kg dry weight. Biogeochemical cycling of elements especially Mn was studied in anoxic lake
sediments by various authors. According to them recycling of Mn was very close to the sediment-water interface and high Mn deposition during summer [75,76,77].

**Manganese in fish**

Galtsoff [78] reported that the heavy metal concentration in oysters were in the order Zn >> Fe > Cu > Mn > Ni. Patel et al [20] observed seasonal changes in natural metal concentrations in marine biota and concluded that the bioaccumulation was high during summer season. Stumm and Bilinski [79] have proved that no clear relationship existed between concentrations of Mn in water and fish tissue which was due to the formation of weak organic complexes on the Mn in water phase [20] or due to redox conditions [80]. On the other hand, it was suggested that the higher concentration of Mn in fish tissues were taken from food or sediment [81,82]. Paul and Pillai [83] observed that bone of fish contained a higher concentration of Mn.

1.1.5 Zinc

Zn is one of the most abundant essential trace elements in human body. It has the ability to occupy the low symmetry sites in enzymes and is necessary for functioning of various enzyme systems including alkaline phosphatase, carbonic anhydrase and alcohol dehydrogenase. It is also a cofactor for several enzymes. Reid and Wood [84] have classified Zn as a very toxic and easily accessible heavy metal. Zn is a component of Zn containing blood pigment hemosyscotypin in molluscs [3]. The clinical effects of Zn deficiency include growth retardation, male hypogonardism, rough skin, poor appetite and mental lethargy [85].

**Zinc in water**

According to WHO [86] Zn in drinking water possesses astringent taste, opalescence and sand like deposits. The desirable level is 5.0 mg/l with a maximum allowable limit of 15 mg/l. Normally in fresh water, the levels of Zn ranges from 0.005
to 0.015 mg/l. However higher values have been recorded near industrial areas [45]. Paul and Pillai [13] found the concentration of Zn in Periyar River water to range from 0.05 to 7.50 mg/l. The wide fluctuations were attributed to seasonal and discharge variations. The total and filterable Zn content in the Yarra River was found to range from 24-89 and 15-55 mg/l respectively. As the river enters the estuary, a significant increase in the average total metal concentration for Zn was noted. This increase is attributed to the particle fraction. In contrast a significant reduction in the average total metal concentration of Cu and Fe was found [57]. Saikia et al [87] reported Zn content in upper Ganga water to range from 0.0987 - 0.1366 mg/l.

Zinc in sediments

Jones and Jordan [61] reported a range of 166-1280 mg/kg dry weight in sediment from the river Liffey estuary in Dublin. Grieve and Fletcher [60] have reported Zn content for suspended sediments from the Fraser River Estuary in British Columbia to range from 150-542 mg/kg dry weight. The mean Zn concentration in fresh water sediments of Coeur d'Alene Lake, Natural Creek and Illinois River (U.S.A), Derwent Reservoir (U.K) and Yellow Knife Bay (Canada) were found to be 3800, 1045, 81, 1035 and 200 mg/kg dry weight respectively [52, 53, 54, 88, 55]. Paul and Pillai [13] reported a high concentration (upto 5500 mg/kg dry weight) at the outfall areas in Periyar River.

Zinc in fish

Brooks and Rumsey [89] reported that the average concentrations of Zn in muscle, liver, kidney, heart, gonad, spleen and gill of eight species of New Zealand Sea fish were 8, 76, 78, 24, 93, 73 and 22 mg/kg fresh weight respectively. Mackay et al. [39] reported that the ratio of Zn in liver to muscle of black marlin was 5.5:1. Zn in muscle tissue from 15 species of omnivorous and carnivorous fish collected from industrial and agricultural areas of the lower Great Lakes were 16-82, 3-9 mg/kg fresh weight respectively [90]. Yellow Perch, Blue Gill and Black Crappie inhabiting recreational and industrial zone rivers in the U.S.A. had average muscle burdens of 106, 108, 103, 100, 109 and 101 mg/kg dry weight respectively [91,92].