Trace Metals in the Environment

Trace metals are intrinsic, natural constituents of our environment. Apart from the natural sources, several anthropogenic ones also contribute to metal concentrations in the environment. Some of the anthropogenic sources of the metals in the environment are: mining, smelting, production and use of the compounds and materials containing the metals, burning of fossil fuels, waste dumping and leaching of waste dumps, urban run-off, sewage effluents and agricultural run-off. Toxic metals to a large extent are dispersed in the environment through industrial effluents, organic wastes, refuse burning, transport and power generation. They can be carried to places many miles away from the source depending upon whether they are in the gaseous form or as particulates. Another means of dispersal, especially in the hydrosphere is the transport of the effluent from catchment areas which have been contaminated by wastes from various industries.

The study of toxic and trace metals in the environment is more important in comparison to other pollutants due to their non bio-degradable nature, accumulative properties and long biological half lives. It is difficult to remove them completely from the environment once they enter into it. With the increased use of a wide variety of metals in industries and in our daily life, there is now a greater awareness of toxic metal pollution of the environment. Many of these metals tend to remain in the ecosystem and eventually move from one compartment to the other within the food chain.

There is considerable concern about the human health aspects of metal cycling in polluted coastal and inland waters that are in proximity to large population centres. In hydrosphere, trace metal concentrations are typically orders of magnitude greater in the sediments as compared to those in overlying waters. The capacity of the sediment to concentrate trace levels of most of the metals make them useful indicators for monitoring purposes and for detecting sources of pollution in the aquatic system. The analysis of sediment cores may provide a historical record of the heavy metal burdens. Determination of elemental concentrations in the aquatic organisms provide information about bio-accumulation and bio-magnification processes. Many organisms including plankton and fish, indeed, act as bio-monitors. Compared to the sediments, marine organisms often exhibit greater ability to accumulate metals from the water column and are hence more useful for identifying the sources of contamination [5].

Extensive studies were carried out in our laboratory, over the years, on the metal pollution in Thane creek which acts as a major sink for various municipal wastes and industrial discharges from the adjoining areas. The industrial wastes not only pollute the creek waters but also pose a threat to the aquatic biota. Three locations in the creek were selected on the basis of effluent discharges and samples of water, sediment and biota collected and analysed. Salient results of these investigations are presented and discussed in this paper.

Thane Creek : A Profile

Thane Creek (TC), which is adjacent to Mumbai harbour bay, lies between latitude (19.5°N-19°N) and longitude (72.5°E-73°E). It is a triangular mass of brackish water which widens out and opens to the Arabian Sea in the South. The creek is narrow at the Northern end, where it is fed partially by river Ulhas. Along the east and west sides of the creek, many industrial units have come up. Thane creek is the ultimate recipient of all the liquid discharges from these industries. The discharges into the creek on its Western side are dominated by Mumbai city sewerage and effluents from the industrial complexes, including the textile mills of South and Central Mumbai, the petrochemical, fertilizer and thermal
plants at Chembur and the pharmaceutical and chemical complexes at Vikhroli, Bhandup and Mulund. The Trans-Thane Creek Industrial Area was developed as a chemical zone by the Maharashtra Industrial Development Corporation. The area houses a number of major, medium and small scale industrial units largely involved in the manufacture, storage and use of chemicals, petrochemicals, pharmaceuticals and fine chemical products, pesticide formulation, etc. Of the 1800 odd industries registered in the area, nearly 50 could be termed as major and the rest classified as small and medium scale. The effluent discharges both treated and untreated are let into the creek.

Results and Discussions

Concentrations of metals in creek water:

Concentrations of toxic and trace metals like As, Ca, Cd, Cu, Fe, Hg, Li, Mg, Mn, Pb and Zn in creek water from the three locations showed a large variation. The toxic metals like Cd, As, Hg, etc., were found to be in ppb (ng/ml) levels while the metals like Ca, Mg, Fe, etc., were present in ppm (µg/ml) range reflecting their origins. In general, the concentrations of metals found in this study were 3-8 times higher than ambient values measured in unpolluted Indian coastal waters (Cu: 1-25 µg/l, Fe: 2-16 µg/l, Mn: 1-8 µg/l) [3]. The distribution of Ca, Cd, Cu, Fe, Mg, Mn and Zn in the water samples from Airoli, Vashi and Trombay sites is shown in Fig. 1. It is evident from the figure that the levels of these metals increase from north to south from Airoli to Trombay. This is due to increased industrial effluent discharges as one moves south from Airoli.
Concentrations of metals in sediments: Metals are not necessarily fixed by the sediments permanently, but may be recycled via biological and chemical agents both within the sedimentary compartment as well as in the water column. Behaviour of trace metals in the coastal marine sediments is largely related to their capacity for complexation with organic matter in truly dissolved, colloidal, macro particulate phases.

The distribution of metals Ca, Co, Cr, Cu, Fe, Mg, Ni and Pb in sediments at Airoli, Vashi and Trombay sites is shown in Fig. 2. It is seen from the figure that in general these concentrations decrease as one moves south from Airoli to Trombay. The concentration of toxic metals such as Cd, As and Hg in these sediments were similar at the three locations and were in the range of 0.1-0.3, 2-2.3 and 0.8-1.4 µg/g, respectively.

Concentrations of metals in suspended solids: Sediments get into the hydrosphere from the atmosphere, rivers and streams, glacial activity and ground water. Within the ocean, and to a lesser extent in lakes, the sediments move with the water, there being a critical velocity of a water current below which a particle will settle, and above which the particles are transported. At the reduced flow rates and low velocities, suspended particulates settle down and get incorporated into the sediments. The chemical composition of the sediments reflect that of the overlying water column.

The suspended solids concentrations in Thane creek water were also measured at the selected locations. The levels were 13.6, 19.8 and 30.7 mg/l, respectively. In general, the levels of metals in suspended solids were found to be higher at Trombay site than those at Airoli and Vashi which can be attributed to increasing contributions from industrial effluents as one moves from Airoli to Trombay.

Concentrations of metals in biota: The aquatic environment is extremely variable and there are many factors which modify the effect of an element on the biota. The aquatic system near the industrialized areas contain large amount of heavy metals, which have marked ecological significance due to their toxicity, persistence and bio-accumulation.

![Fig. 2 Concentrations of metals in sediments at different locations in Thane Creek](image)
Persistence of trace metals in the environment may have possibilities for environmental transformation into more toxic compounds. Any toxic compound accumulates in the biological system only when its rate of uptake exceeds the rate of elimination. The toxic compounds enter into the body of the organism from the surrounding medium and is accumulated in certain tissues by the phenomenon of bio-accumulation. Concentrations of trace metals in biota samples from different locations in Thane creek were estimated. The levels of toxic metals in fish and crab samples are given in Fig. 3a and Fig. 3b, respectively. It is seen that the levels of major metals Ca and Mg are higher by a few orders of magnitude in comparison to toxic metals such as As, Cd, Cr, Pb and Hg. The levels of toxic metals in crab samples are much higher than those in fish samples.

It is known that cationic elements in general follow co-precipitation with MnO₂ colloids, and anionic elements follow co-precipitation with Fe(OH)₃ colloid. A correlation between Co with Fe(OH)₃ and Ni with Mn in Mn nodules from deep sea has been established [2]. In Thane creek sediments, Co to Fe ratio varied in the narrow range of (3.9-4.4)x10⁻⁴ where as in fishes the variation was over a much higher range.
This shows that some fish species can preferentially concentrate Co as compared to Fe. In our earlier study [4], it was found that upto 95% of total mercury in fishes was associated with organic component (methyl mercury). The higher concentrations of heavy metals in Thane creek area due to liquid effluent discharges from industrial units situated on the shores show a possible organic association and there is, therefore, a need to determine the organic fractions of all these metals in Thane creek waters and marine organisms.

**Transfer factor of metals**: The 'Transfer Factor' is the ratio of the level of the trace element in the concentrating matrix (e.g. fish) to the concentration in the ambient matrix (e.g. sea water) under equilibrium conditions. The transfer factor is a general term and there are many specific terms used to describe the transfer between two typical matrices. Concentration by physical, chemical and biological processes is represented by a number generally known as 'Concentration factor'. This concentration factor is also a general term whereas other specific terms as bio-accumulation factor (Bp) and distribution coefficient (Kd) for biota and sediments are used.

**Distribution coefficient (Kd)**: Coastal marine sediments are a major repository as well as potential source of trace metals. Sediments are sinks for many inorganic and organic pollutants transported through the water column from various sources. Due to their particle reactivity, trace metals tend to accumulate in sediments [1], and, as a result, may persist in the environment long after their primary source has been removed. Distribution coefficient is expressed as the ratio of the concentration of an element in the sediment in (g/kg) dry weight to the concentration of the element in sea water in (g/L) under equilibrium conditions. The distribution coefficients of different metals at different locations in our study area were calculated. A wide range in Kd values were observed for different metals. The Kd values (L/Kg) for major metals like Mg, Ca varied between 16 and 128. Maximum Kd value of 5.5 x 10^3 was observed for Fe at Airoli site. The Kd values for highly toxic metals like As, Hg, Cd and Li varied between 237 and 952, while the maximum Kd values for the metals of industrial importance like Cu, Mn, Pb and Zn observed at these locations were 2180, 4500, 8409 and 8000, respectively. The distribution coefficients of industrially important metals are given in Fig. 4. The variation in Kd values of different metals can be attributed to the solubility of the metal in water (less soluble is the metal, higher will be the Kd value) as well as contribution of industrial source at a specific site.

![Fig. 4 Distribution coefficient of industrially important elements in sediment at Thane Creek](image)

The mean distribution coefficients (Kd) for sediments in our study area were in the increasing order of 535, 1482, 4015, 5670, 5833, 3.6 x 10^3 for Cd, Cu, Mn, Pb, Zn and Fe, respectively. The bio-accumulation factors observed for marine organisms in the creek for Pb, Cu, Cd, Fe, Mn and Zn were 67, 387, 557, 1260, 2187 and 4172, respectively. It is clear that Pb is relatively more enriched in sediments compared to that in fishes.

**Bio accumulation factor (Bp)**: Metal concentration in the sediments does not represent the metal bio-availability. Metals are accumulated in certain organs of various biota. However, not all organisms accumulate metals and not all metal accumulating organisms can serve as bio-monitors because some organisms are capable of maintaining a fixed body regulated trace metal levels irrespective of the sediments. High metal concentrations pose danger to the organisms especially to those living on the sediments and which enter the food chain. Bp is
expressed as the ratio of concentration of a metal in the organism in (g/kg) wet weight to the concentration of the same in sea water in (g/L) under equilibrium conditions.

The bio-accumulation factors for Ca, Cd, Cu, Fe, Mg, Mn, Pb, Zn, As and Hg for fish and crab were calculated for the three sites and are plotted in Fig. 5.

The large variation seen in accumulation factors can be attributed to type of biota, age of biota, local industrial sources and chemical nature of the metal. In general, higher bio-accumulation factors were observed for crab samples for all sites as compared to fish.

**Correlation between Metals**

Elements which are strongly correlated at a receptor site indicate a likelihood of similar originating sources, size fraction and/or transporting agencies from source to receptor site. The correlation matrices for different trace metals for sediment, water, suspended solids and biota samples were calculated. A typical correlation matrix for suspended solids in water samples for Trombay region is given in Table-1. It is seen that a good correlation exists among major metals, namely, Ca, Mg, Fe, Mn and Zn. A good correlation of Pb with Cu and Cr as well as Cr with Cu indicate the contribution of these metals from industrial sources. In sea water samples from Vashi, a good
correlation among major metals, i.e. Ca, Mg, Fe and Mn, was also observed.

Daily intake of metals through marine food for Mumbai population was calculated. An average daily consumption of 14 g of marine food was taken for this purpose with a wet to dry mass ratio of 3.7. The daily intake of metals from ingestion and inhalation pathways were reported in our earlier studies [6,7,8]. The daily intake of toxic metals like As, Cd, Hg, Mn and Pb through fish worked out to be 0.25, 0.22, 0.42, 52.9 and 0.57 µg, respectively. The contribution of marine component to the total intake of these metals works out to be 2.58, 8.15, 3.36, 2.39 and 1.61%, respectively which is not significant.

References