DISCUSSION

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Physico-chemical studies of water qualities are an important aspect from the point of view of aquatic biology (Tebutt, 1992). The abnormal physico-chemical characteristics of industrial effluents are responsible for the fish kill (Mishra, *et. al.,* 1988). Water quality can have great influence on the ability of aquatic organisms to grow and exist (Pawar and Mane, 2006).

The Physical parameters like temperature, salinity were studied during present investigation. During chemical investigation major chemical parameters namely pH, dissolved oxygen, free carbon dioxide, nitrate, phosphate were studied.

All the physicochemical parameters such as temperature, pH, salinity and dissolved oxygen (DO) showed well marked variations, being influenced by monsoon cycle. Marichamy, *et. al.,* (1985) reported monsoonal influence on the physicochemical parameters of the coastal waters.

Temperature is one of the most important abiotic parameters that regulate the self purification capacity of rivers and reservoirs and hence measurement of water temperature is vital importance in the field of limnology for calculating solubility of oxygen, carbon dioxide. Many biological processes that occur in marine and estuarine waters are sensitive to temperature changes. Water salinity and temperature are the most important physical factors affecting the activities of marine and estuarine organisms, marine and estuarine waters. They affect every physical property of seawater. (Cox 1965).The processes of the chemical, petrochemical, pulp and paper industries; municipal sewage; and thermal power generating stations affect the temperature (Swiss, 1984).

Temperature affects many chemical and biological processes. Chemical equilibrium constants, solubilities, and the rates of chemical reactions are temperature-dependent (Whitehouse, 1984). Most marine and estuarine organisms are poikilotherms. As a result, biological processes, such as photosynthesis and respiration rates, spawning, uptake of toxic substances, and behavioural patterns of organisms, are all responsive to changes in temperature (Strickland, 1965; Houston, 1982; Aiken and Waddy, 1990).

A comprehensive review of the effects of water temperature on marine and brackish water animals was conducted by Kinne in1963. The results of this review indicated that the biological processes may be greatly affected by water temperature fluctuations. Most of the marine and estuarine species, or populations within species, have characteristic tolerable temperature ranges (Canadian Environmental Quality Guidelines 1996).

The temperature changes can significantly affect the rate of respiration; susceptibility to disease; osmoregulation; uptake of pollutants; susceptibility to the toxic effects of pollutants; various behavioral patterns, including physical activity, reproduction, feeding, growth, distribution, intra-and inter-specific competition, predator–prey relationships, community composition, and parasite–host relationships; and many other biological processes (Kinne, 1963).

The sensitivity of aquatic organisms to toxic substances increases with increasing water temperature (Cairns, *et. al.,* 1975). The interactions between temperature and toxicity, is however very complex. Voyer and Modica (1990), reported that as water temperature increases, the rate of metabolic processes increases, resulting in enhanced uptake and toxicity of metals to marine and estuarine organisms (Phillips,1976; Waldichuk, 1985; McLusky, *et. al.,* 1986; Voyer and Modica, 1990).

In the present study, estuarine water generally tended to be warmer during the summer season (March to May). In the summer season peak values were obtained from April to May. The maximum air temperature was recorded during the summer season, owing to the clear sky with more solar radiation. Less solar radiation with cloudy sky and more rainfall during the monsoon season greatly reduced the air temperature Kannon, 1992; Ganesan, 1992; Sampath Kumar, 1992; Saraswathi, 1993). Tampi (1959) noticed the annual cycle of temperature variation at Mandapam. Marichamy, *et al.,* (1985) noticed that, both the air temperature and surface temperature steadily increased from winter (low level) to the spike level during summer (April - May) in the Gulf of Mannar region. In winter season the climatic changes and a deduction in incoming radiation may lower the temperature.

There is relation between temperature of water and chemicals present in the effluents. Chemicals exerts their antagonistic influence on the feeding rates of fishes at high temperature by acting on enzymatic or metabolic depressors that are responsible for suppression of feeding rate of fish (Sarkar, 1997).

The increase in the temperature was affected directly by increase in toxicity and deoxygenation, produced by the biological oxidation of organic matter (Rajlaxmi and Sreelatha, 2005). Quadrose, *et. al.,* (2001) reported wide fluctuations of water temperature between 17 ^{0}C to 35 ^{0}C in Thane Creek (India). According (Mishra, *et. al.,* 1993) most of the Indian estuaries exhibit temperature difference of 8 ^{0}C to 10 ^{0}C.

In the present study temperature of water samples showed variations in the range of 26 ^{0}C to 30 ^{C}C from three stations. Slight rise in temperature at station A was associated with increased sources of industrial pollution.

The atmospheric temperature generally varies between 10 ^{0}C to 35 ^{0}C in a year. The measurement of temperature in water is important basically for its effect on the chemistry and bio-chemical reactions in the organisms. Chauhan and Saxsena (1992) observed that toxicity of heavy metals increases as the temperature increases.

The pH of water gets drastically changes with time because of exposure to air, temperature changes and biological activities. Significant change in pH occurs due to disposal of industrial wastes and acids in drainages (Trivedy and Goal, 1986).

The pH of natural water varies around seven generally seven (i.e. alkaline). High pH is unfavourable to aquatic organisms (Das, 1978). Munshi (1980) reported effect of low pH on the gills of *Channa punctatus*, suggesting that, low pH medium interfere in gaseous exchange, structure of gill and it's respiratory function.

Karanjkar (2001) reported that, pH of various industrial effluents ranged from 3.0 to 10.1. The textile mill effluent and tannery effluents are alkaline with high pH; while that of electroplating effluent is acidic with low pH. These values are similar to those reported by Mishra and Saksena, (1989); Pandey, *et. al.,* (1993).

pH of the estuarine water fluctuated between summer (Feb - May) and post monsoon (Aug - Nov.). Abhaykumar, *et. al.,* (1995) also reported that, the increased pH level observed during summer might be due to the water evaporation and high salt accumulation in the estuary.

The pH of water is an important indicator of the physico-chemical conditions of estuarine environment. The pH ranged from 6.8 to 7.9, low during the monsoon in Thane

Creek (India) (Quadrose, *et. al.,* 2001). The pH ranged 6.70 to 7.58 in Kadinakulam Estuary, Southern Kerala (Arunkumar, and Joseph, 2006).

In present investigation all pH values indicates acidic nature of water and ranged from 5.15 to 7.90. The maximum pH (7.90) was recorded in the month of November, 2008 while minimum (5.15) in the month of April, 2008, at Station A, indicates change in the nature of water it might be due to receiving the industrial effluents from the industrial area.

The toxicity of heavy metals might be more at these levels. Toxicity of heavy metals like Al, Cd and Fe on hatching of eggs and survival of larvae of Zebra fish *Brachydono rerio* was studied at different pH (4-9) by Dave and Goran (1985) and found that, Aluminium and Cadmium were more toxic at high pH level, while iron was more toxic at low pH. The hatching was stimulated when pH was lowered from 7 to 6 but further lowering of pH retarded hatching.

Alam, *et. al.,* (1991) reported that water samples from selected industrial drainage and receiving streams in and around Islamabad, Pakistan, during summer of 1987-1990 showed disturbances in pH and oxygen level. Karanjakar (2001) reported that, pH of various industrial effluents ranged from 3 to 10.1. The increasing pH is an indicator of high phytoplankton productivity to a certain extent was reported by Zingade and Desai (1989).

The pH was quite low during floods in the peak monsoon season due to the influence of freshwater influx, dilution of saline water, reduction of salinity and temperature and decomposition of organic matter (Ganesan, 1992). Many Indian rivers polluted due to industrial effluents have variety of pH ranging from acidic to alkaline (Mishra, and Saksena, 1988; Rana and Palria, 1982; Palria and Rana, 1985).

Carbon dioxide is commonly found in water from photosynthesis and decomposition of organic matter. Excessively high levels of Carbon dioxide (Greater than 20 ppm) may interfere with the oxygen utilization by the fish. Sawane, *et. al.,* (2006) reported the inverse relationship between pH and Carbon dioxide.

In present study, the minimum concentration of free carbon dioxide (3.00 mg / l) was recorded at Damandevi (Station C) in the month of March, 2008 and maximum

(76.15 mg / l) at Kotawali (Station A) in the month of July, 2008. The free carbon dioxide values were extremely high at Station A (76.15 mg / l) and Station B (54.00 mg / l).

Carbon-dioxide accumulates in water due to microbial activity and respiration of organisms. In summer, with increase in atmospheric temperature, there was corresponding rise in water temperature and consequent increase in biological oxidation of organic matter that might have caused an elevation in level of carbon dioxide (Singh and Srivastava, 1988).

The high carbon-dioxide level indicates pollution of water body. Jesudas and Akila (1995) studied free Carbon-dioxide from sugar factory effluents and industrially polluted lake.

The amount of carbon-dioxide depends on the decomposition of top soil and chemical nature of the underlying rocks (Mann, 1958). Free carbon-dioxide in water may be due to enhanced rate of decomposition of organic matter or respiratory activities of aquatic in – habitants. High carbon dioxide content may change aquatic body into acidic nature through development of weak carbonic acid (Freeda, *et. al.,* 2001).

Dissolved oxygen (D.O.) is very important parameter to assess the quality and is an index of physical and biological processes going on in the water. The sources of oxygen in water are mainly by two ways, either from air or from photosynthetic activities.

Dissolved oxygen is a key parameter reflecting the quantity of water and hence used in classifying the water quality, which receives the wastes. Its presence is essential to maintain biological life in water.

Dissolved oxygen is one of the important factors in water quality assessment. Its presence is essential in aquatic ecosystem in bringing out various biochemical changes and its effects on metabolic activities of organisms. The oxygen balance of the system largely determines the effects of waste discharged in water body. Non - polluted surface waters, remain saturated with dissolved oxygen. Dissolved oxygen levels in natural and waste waters are dependent on physical, chemical and biological activities primarily by three factors – i) Free diffusion of atmospheric oxygen, ii) Oxygen production through photosynthesis, and iii) Dissolved oxygen consumption by plants, animals and decomposers.

The quality of dissolved oxygen in water is directly or indirectly dependent on water temperature, partial pressure of oxygen in the air, concentration of dissolved salts, amount of chlorophyll content etc. (Welch,1952) and temperature and hydrogen ion concentration (Wetzel, 1975). For diversified warm water biota, the dissolved oxygen concentrations are at least 5 mg / l.

Non - polluted surface waters are normally saturated with dissolved oxygen. Mishra and Saksena (1989) studied the physico-chemical parameters of the industrial effluents from textile mill in Birlanagar, Gwalior.

In present study, maximum DO was recorded in August, 2008, 10.72 mg / l, at Dhamandevi (Station C) while minimum in February, 2008, 4.48 mg / l, at Kotawali (Station A). The dissolved oxygen was as recorded at minimum levels in the month of February, 2008 at all three stations.

The hike in the level of oxygen might be due to the effect of monsoon and climatic conditions such as, low solar radiation prohibited by the clouds, land water run off and higher wave action, although the rate of photosynthesis is reduced. In summer months decaying organic matter, increased temperature and the absence of string winds seem to be the contributing factors for low level of oxygen in this season (Tampi, 1959). Wind and wave action produce through aeration of the surface waters (Rao, 1967). Kannan and Kannan (1996) reported maximum DO concentration during the monsoon / post monsoon season, which was due to the photosynthetic activity of phytoplankton and renewal of water consequent to monsoon rains.

DO was observed to be low during summer season, which could be attributed to high temperature and high salinity of the water, similar results were obtained by Marichamy, *et. al.,* (1985).

The dissolved oxygen and organic matter have a negative relationship which might due to utilization of oxygen for oxidation of organic matter Paka and Rao, (1997).Similar observation was recorded by Bharati and Murthy (1990); Kumar and Sharma (1999) in Sengar river at Shikohabad (Uttar Pradesh), Which receives effluents from paper mill, Pande, (2001) in river Ramganga at Moradabad industrial Complex, Deshmukh and Ambore, (2006) in river Godavari at Nanded M.I.D.C. area.

The dissolved oxygen in industrial effluents remains too less (Kumar, *et. al.,* 1974; Ramaswamy, *et. al.,* 1982; and Trivedy, *et. al.,* 1986). Many substances are more toxic when dissolved oxygen of the water is reduced (Cairns, *et. al.,* 1975). The release of biodegradable pollutants from domestic and industrial sources stimulates growth of micro-organisms which consumes the dissolved oxygen of water (Bath and Kaur, 1999).

The salinity of coastal waters is also vital because of the physical and chemical interactions that may occur with stress factors and toxicants. The solubility, uptake, and bioavailability of certain compounds in aqueous media, these are the physical interactions can be affected by salinity. Salinity can regulate the quality of water and determines the extent of dissolution of gases, hydrogen ion concentration and other characteristics of brackish water. In accordance with Jayaraman's report (1954) water current is the most relevant factor governing the seasonal distribution of salinity. The main factor seems to be the rainfall which reduces the salinity by the admixture of freshwater brought down by the river and canals.

Salinity levels in coastal waters shows variations because of river inputs, influx of groundwater, freshwater runoff with rainfall, variable evaporation rates, and tidal and ocean currents (Harrison, *et. al.,* 1983).Many semi-enclosed areas and estuaries show extreme salinity variability in time and space (Krauel, 1975; Thomson, 1981; Dickie and Trites, 1983; Prinsenberg, 1986; Smith, 1989; Hopky, *et. al.,* 1990).

The freshwater diversions, large volume of industrial and municipal effluent discharges, and barriers to existing flow patterns by anthropogenic contribution can change the salinity of estuaries and other coastal water bodies and affect the biota (Thomson, 1981; Dickie and Trites, 1983).

In estuarine organisms changes in the salinity with tidal cycles would be the important factor in relation to the metal toxicities. The toxicity of various pollutants and sensitivities also related with variation in temperature in estuarine organisms. Generally temperature increase reduces the period of survival of fish in lethal concentrations of toxic substances (Bodrova and Kraiukhin, 1956).

Quadrose, *et. al.,* (2001) recorded the average salinity of 4 ppt in Thane Creek (India). The higher Salinity of 31.36 mg / l was recorded in Kadinakulam Estuary, Southern Kerala (Arunkumar, and Joseph, 2006).

From the data it is seen that, the Fluctuations in salinity ranged from 0.04 to 6.00 ‰ at all the three stations. The salinity increases during the months when rainfall is scarce and the maximum during the period extending from March to May. High salinity were recorded from March to May, could be attributed to high degree of evaporation of surface water. Low salinities were recorded during the months of June to November. Due to the heavy rainfall all the physicochemical parameters were changed, especially it can inversely affect the salinity. The percentage of salinity lowered during monsoon period. Due to heavy rainfall in monsoon, the salinity was gradually decreased and minimum salinity was recorded in August.

In aquatic ecosystem Phosphate-P plays an important role as a nutrient along with nitrates, domestic sewage, industrial effluents, detergents which are main sources of phosphates in water. The phosphate contents in these effluents after reaching the receiving water body may lead to significant undesirable growth of the planktons and other weed species leading to organic pollution of water body. Inorganic phosphorus is one of the most important nutrients limiting growth of autotroph and thus biological productivity of system. Industrial effluents, domestic sewage, detergents are main sources of phosphates in water.

Alam, (1993) recorded PO_4-P content of 0.00 to 4.38 mg / l at Malad creek. Ramakrishna, *et. al.,* (1987) recorded PO_4-P content of 15- 40 mg / l, in Ollipuiramkadavu back waters. Sarala Devi, *et. al.,* (1991) reported maximum PO_4-P content of 0.383 mg / l, for Indian estuaries. PO_4-P content ranged between 0.21 to 2.31 mg / l in Kadinakulam Estuary, Southern Kerala (Arunkumar, and Joseph, 2006). According to Ketchum, (1967) PO_4-P limit for unpolluted water as 0.09 mg / l.

In present study, the phosphate content was maximum of (12.50 mg / l) in the months of December, 2007 and September, 2008, while minimum phosphate content of (2.21 mg / l) in the month of March, 2008 was recorded at Kotawali (Station A).The average phosphate content at all three stations was high and water was more polluted at Kotawali (Station A).

Karanjkar (2000) detected average phosphate concentration from effluents of textile mill; electroplating and tannery were 0.319, 0.337 and 0.202 mg / l respectively. The phosphate contents in these effluents after reaching the receiving water body may lead to significant undesirable growth of the plankton and water weed species leading to organic pollution of water body.

Nitrates are the highest oxidized form of nitrogen. It is contributed to surface water to a large extent, by sewage and industrial effluents and also due to biological fixation and oxidation of organic matter. The run off water coming from intensive agricultural activity (involving the use of fertilizers) also significantly contributes to the higher nitrate content in water is an indication of pollution.

Quadrose, *et. al.,* (2001) recorded the Nitrate- Nitrogen was ranged 0.01- 92 mg / l and average of 17.82 mg / l in Thane Creek (India). Nitrate- Nitrogen content for Indian estuaries was 0.00 to 1.96 mg / l (Sarala Devi, 1991). Nitrate- Nitrogen was ranged 0.0008 – 2.24 mg / l in Kadinakulam Estuary, Southern Kerala (Arunkumar and Joseph, 2006). According to Varshney (1985) more than 1.26 mg / l of NO_3-N indicates polluted condition of water.

In present study, the values of nitrates ranged between 1.24 to 48.75 mg / l. It ranged from 3.27 to 47.50 mg / l at Kotawali (Station A), from 1.48 to 48.75 mg / l at Songaon (Station B) and from 1.24 to 17.50 mg / l at the Dhamandevi (Station C). The average nitrate content for Kotawali (Station A) was 21.11 mg / l through out the year. As compared to the Station B and Station C the average nitrate content for Station A was high, probably due to organic flow from industries. The values of nitrate concentration at Station C were within the limit of ISI desirable standard (25 mg / l) (Horne and Goldman, 1983).

Bath and Kaur (1999) detected the nitrate content of water sample collected from industrially polluted, Budda-Nallah, Ludhiana, Punjab, ranged between 3.0 to 15 mg / l. Choudhari and Bharati (2006) noticed maximum nitrate concentration (92.05 u / l) in industrial waste water, influenced by printing and dying units.

Activities of human directly pollute the water with pesticides, crude oil, and other chemical run-off from factories. Generally aquatic animals and fishes in particular from polluted waters get affected in various ways. Fishes may suffocate due to surface water, covered by oil, thereby physically preventing free exchange of gases.(Daniels, 2002).Water pollutants includes many toxic chemicals coming out of sewage, industrial effluents, garbage, insecticides, pesticides, fertilizers etc. are lethal to fishes, acting directly on gill filaments. Some of them are neurotoxic like Lead (Anonymous, 1982).

The industry continues to be one of the most significant causes of pollution of aquatic ecosystems due to adverse kind of wastes produced by treatment limited due to higher toxicity levels and the risks associated with exposure to wild life. (USEPA, 1993)

The heavy metals have a great ecological significance because of their accumulative behavior and toxicity. Water pollution affects fish health with toxic metals, which resulted from accidental spillage of chemical wastes, periodic precipitation contaminated with air-borne pollutants, discharge of industrial or sewerage effluents, domestic waste water, and agricultural drainage etc. (Handy, 1994; Jent, *et. al.,* 1998). Fish health is also affected by pollution of heavy metals, which occurred due to contamination of water with fertilizers containing heavy metals (Chaisemartin, 1983).

Heavy metals are those having density 5 times higher than that of water. They are usually present in trace amounts in water, but many of them are toxic even at very low concentrations. Their concentration increases due to addition of industrial wastes and domestic sewage (Trivedy and Goel, 1986). Presence of many metals at the trace levels in the human environment has received increasing global attention (WHO, 2002; IRPTC, 1984).Heavy metals such as mercury and cadmium uptake by fishes and prawns, when present in low concentration in the water, may be restricted by strong complexing agents in mucous layer (Part and Lock, 1983).

In the environment, heavy metals occur both as a result of natural processes and as pollutants from human activities (Garcia-Montelongo, *et. al.,* 1994; Jordao, Pereira, *et. al.,* 2002).

In marine ecosystems, accumulation of heavy meals is of global importance. Metals generally enter the aquatic environment through of geological matrix or due to anthropogenic activities, domestic sewage, and mining waste and atmospheric deposition.

The heavy metals are persistent and stable environmental contaminants of aquatic environments. Some metals like Zn, Cu, Fe and Mn, which are required for metabolic activity in organisms. Heavy metals like Cd, Hg, Cr and Pb, may exhibit toxicity even at low levels under certain conditions. Thus there is necessity of regular monitoring of sensitive aquatic environments (Cohen, *et. al.,* 2001; Fergusson, 1990; Peerzada, *et. al.,* 1990).

Some metals like copper, chromium, zinc, tin and mainly heavy metals like arsenic, cadmium, lead and mercury are widely used in various industries such as in processes related to batteries, metal works and electronics. These metals are also used in manufacturing of certain medicines, glazes, inks, pesticides, paints and pigments etc.

The high amount of these materials would usually carried by wastes of these industries. These are extremely toxic as ions, and cannot be recovered or degenerated, once dispersed in the biosphere. Such water pollution by these chemicals leads to many abnormalities including stunted growth, skin ulceration, and reproductive failure in fish fauna. The other tolerance danger is that the fishes accumulate toxic substances in their tissues without any external symptoms. (Bhilave, *et. al.,* 2004) The predators of these fishes such as birds and humans are the most vulnerable to a chain of influence (Daniels, 2002).

The occurrence of elevated levels of trace metals mainly in the sediments can be a good indication of man induced pollution and high levels of heavy metals can often due to the anthropogenic influences. The analysis of heavy metals in the sediments permits detection of pollutants that may be either absent or low concentrations in the water column and their distribution of costal sediments provides a record of pollution in particular region or ecosystem (Davies, *et. al.,* 1991).

The heavy metal concentrations in water column are relatively low, but the concentrations in the sediment may be elevated. Heavy metals are known to accumulate in the sediments, which act as sink for these pollutants (Martin and Whitfield, 1983)

In India various scientists have studied metal pollution. Many investigators have detected increasing trend of heavy metals in marine environment. It has been also shown that marine prawns, crabs, clams and fishes carry heavy metals in various degrees (Alagarswamy and Narsimhan, 1973; Tejam and Haldar, 1975; Sabnis, 1984; Shivaraj and Patil, 1988; Laxman, 1988; Achary, 1988; Appukuttan, *et. al.,* 1988; Evtusheso, *et. al.,* 1990; Joseph and Shrivastava, 1993; Gorden, *et. al.,* 1998).

The heavy metals effects on fish are multidirectional and manifested by numerous changes in physiological and chemical processes of their body systems. (Dimitrova et al., 1994) Pollutants may cause biochemical alterations (Sastry, *et. al.,* 1997) in different organs of fish. Muley, *et. al.,* (2000) reported that significant alteration in the nucleic acids in *Cyprinus carpio* caused due to toxic effects of heavy metals in biochemical level.

In present study, observed range of heavy metals in water samples viz. Cu, Fe, Zn, Cd, Ni, Co and Mn at Kotawali (Station A) they were maximum. Concentration of Copper was 0.046 ppm, Iron content was 0.830 ppm, and Zinc content was 0.370 ppm, Cadmium content were Below Detectable Level, during entire study period except May, 2008 (0.007 ppm). Concentration of Nickel was maximum (0.400 ppm), Cobalt (0.140 ppm), and Mn (40.00ppm) was maximum.

The maximum concentrations of Copper at Songaon (Station B) was 0.013 ppm and at Dhamandevi (Station C) 0.004 ppm respectively. Iron content at Songaon (Station B) was high 0.600 ppm. The maximum (1.950 ppm) concentration of Iron was recorded at Dhamandevi (Station C) Zinc content of water sample at Songaon (Station B) it was 0.330 ppm, while Zinc was below detectable level in the water samples from Dhamandevi (Station C) during study period. Cadmium content at Songaon (Station B): was detected at minimum of 0.001ppm, and maximum 0.008 ppm. The concentrations of Cadmium at Dhamandevi (Station C) were 0.003 and 0.001 ppm. Concentration of Nickel at Songaon (Station B) and Dhamandevi (Station C) was below detectable level during the study period. Concentration of Cobalt in the water samples at Songaon (Station B) was maximum (0.007 ppm), at Dhamandevi (Station C) while it was below detectable level in the water samples collected during the study period. Concentration of Manganese at Songaon (Station B) was 0.032 ppm, at Dhamandevi (Station C) it was only in the months of March,0.008 ppm and April, 2008,(0.006 ppm) during the study period.

In present study, observed range of heavy metals in sediment samples viz. Cu, Fe, Zn, Cd, Ni, Co and Mn at three different stations showed that Ni was below detectable level at Songaon (Station B) and Dhamandevi (Station C) from April to November, 2008.

The level of Copper (Cu) at Kotawali (Station A) was maximum (20.930 ppm) in February, 2008 and minimum (1.960 ppm) in October, 2008. At Songaon (Station B) the maximum copper content was recorded (5.020 ppm) in the month of February, 2008, while minimum (1.100 ppm) in the month of September, 2008. The maximum concentration of Cu at Dhamandevi (Station C) was 5.120 ppm in the month of March and minimum of 0.320 ppm in the month of November, 2008.

Venugapal, *et. al.,* (1982) reported range of Cu concentration of 1.6 to 11.7 ppm / gm in sediment of Cochin back waters. Sahu and Mukherjee (1983) reported loading of toxic heavy metals into the sediment of Ulhas River resulting due to the sinking character of sediment.

Iron (Fe) content was maximum (37.210 ppm) at Kotawali (Station A) in the month of March 2008 and minimum (4.150 ppm) in the month of November, 2008. The concentration of Fe recorded at Songaon (Station B) was high (69.840 ppm) in the month of December, 2007 and low (6.820 ppm) in the month of November2008. The maximum concentration of Fe at Dhamandevi (Station C) was 70.460 ppm in the month of March, 2008, and low (6.520 ppm) in the month of November, 2008.

Zinc (Zn) content was maximum (28.490 ppm) at Kotawali (Station A) in the month of March, 2008 and was minimum (12.430 ppm) in December, 2007.At Songaon (Station B) it was high (25.100 ppm) in March, 2008 and below detectable level in the months of May, 2008 and July, 2008. At Dhamandevi (Station C), level of Zn was high (0.460 ppm) in the month of March, 2008 and was below detectable level in the months of December 2007, and through April, 2008 to November, 2008.

Cadmium (Cd) content of sediment samples was maximum at Kotawali (Station A) in the month of November, 2008 (0.820 ppm), followed by Songaon (Station B) (0.670 ppm) in the month of October, 2008 and Dhamandevi (Station C) 0.650 ppm in the month of June, 2008. The minimum level of Cd content at Kotawali (Station A) during April, 2008 was 0.0029 ppm, at Songaon (Station B) during March, 2008 was 0.016 ppm and at Dhamandevi (Station C) below detectable level for most of the months.

The level of Nickel (Ni) was maximum (0.520 ppm) during the month of March, 2008 in the sediment samples from Kotawali (Station A). It remains below detectable level during the months of December, 2007, May through July, 2008 and October, 2008 the Ni content was below detectable level. At Songaon (Station B) the maximum (0.460 ppm) content of nickel was recorded in the month of March, 2008, and was below detectable level in the months of December, 2007, and May through to November, 2008. For Dhamandevi (Station C) maximum level (0.180 ppm) of Ni was in the month of March, 2008, and was below detectable level in the months of May through November, 2008.

The maximum level (0.710 ppm) of Cobalt (Co) in the sediment samples was from Kotawali (Station A) in the month of May, 2008 and minimum (0.004 ppm) in the month of July, 2008. At Songaon (Station B) the maximum (0.420 ppm) concentration was recorded in the month of September, 2008 and minimum (0.027 ppm) in the month of August, 2008. At Dhamandevi (Station C) Co content was high in the month of March, (0.950 ppm), and was below detectable level in the months of December, 2007, October, 2008 and November, 2008.

Manganese (Mn) content was maximum (112.650 ppm) at Kotawali (Station A) and minimum (12.800 ppm) during October, 2008. At Songaon (Station B) the maximum (113.200 ppm) level of Mn was detected in March, 2008 and minimum 4.480 ppm in November, 2008. At Dhamandevi (Station C) Mn content was maximum (53.120 ppm) during February, 2008 and minimum (4.380 ppm) during October, 2008. At all the stations minimum concentration of Mn was in the month of November, 2008 during the study period.

Heavy metals in sediment exist in different particle – binding phases or different chemical forms. Heavy metals binds with organic compounds, adsorbed in carbonates and oxide minerals, and in the structure of primary and secondary minerals. In environmental studies, the determination of these gives more insight into the mobility, availability, and toxicity for trace metals (Mark, *et. al.,* 1982; Yousef, *et. al.,* 1994).
Heavy metals in water are usually in ionic or colloidal form. They are partly taken in by aquatic organisms into their cells and tissues. The decay of bacteria, plants and animals organic matter is released into water; such water contains certain amount of heavy metals, which further deposited in bottom sediments permanently (Suess and Erlenkeuser, 1975 and Protasowicki, *et. al.,* 1993).

Mitra, *et. al.,* (1999) reported that, concentration of heavy metals in the brackish water wetland ecosystem of West Bengal found to be maximum during monsoon period. High concentration of dissolved heavy metals during monsoon period have been recorded very recently in coastal zone of West Bengal and in present situation there is keen relationship of the Calcutta run off, that bring huge load of heavy metals during monsoon from several factories, electroplating units and tanneries in brackish water wetland of the study area (Mitra, 1999).

Aquatic animals are in direct content with heavy metals both, natural and anthropogenic origin. The discharge of metals by industry represents a serious water pollution problem due to the toxic properties of these elements and their adverse effect on water quality. Golubev (1973) showed that, heavy metals penetrated through the skin and were distributed irregularly in organisms, forming depots. According to Tinsil (1982), there are two ways for penetrating meal in to the organism- via direct water adsorption or fish feed.

Generally it is agreed that, heavy metal uptake occurs mainly from water, food and sediment. Effectiveness of metal uptake from these sources may differ in relation to the ecological needs and metabolism of animals with contamination gradients of water, food and sediment as well as salinity, temperature and interacting factors (Heath, 1987; Langston, 1990; Roesijadi and Robinson., 1994).

Kalfakakcn and Akrida- Demertzi (2000) reported that Ca, Mg, Fe, Cu, Zn, and Pb exhibited bio-accumulation from water to fish.

In present study, quantitative estimation of heavy metal was carried out in locally available and economically important estuarine catfish *Mystus gulio* (Ham.) was done after chronic exposure to the industrial effluents for 30 days at $1/10^{th}$ of LC_{50} value (18 ppm) which was collected from the Lote M.I.D.C. The heavy metals such as Cu, Fe, Zn, Cd, Ni, Co and Mn were detected from the test organs of catfish.

In present study, high concentration of Cu was detected in the liver (0.35 ppm), which was followed by the kidney (0.22 ppm), gill (0.027ppm), and minimum concentration was detected in the muscles (0.011ppm).The observed concentration was below the prescribed permissible limit (30 ppm) by WHO/ FAO (1983).

The high copper concentration in kidney may be due to the fact that fish kidney contains a cystine rich copper binding protein which is thought to have either a detoxifying or storage function (Luckey and Venugopal, 1977).

The high concentration of copper in liver compared to gill, kidney, and muscle can be due to the binding of Cu to the metallothionein in the liver, which serves as a detoxification mechanism (Olafia, *et. al.*, 2004).

Kalay and Canli (1999) reported higher concentration of copper in the liver of *Mugil cephalus* fish from the North Mediterranean Sea.

Observed Iron (Fe) concentration was maximum in the kidney (1.12 ppm) followed by the gill (0.091 ppm), muscle (0.055 ppm), and liver (0.053 ppm).

In present study, the maximum concentration of Zn was detected in kidney (1.47 ppm) followed by liver (0.25 ppm), gill (0.14 ppm), and muscle (0.060 ppm). In present study the Zn was accumulated in gills may be due to the fact that, gills serve as respiratory organs through which metal ions are absorbed (Bebianno, *et. al.*, 2004).

The high level of Zn in liver may possibly reflect storage and also due to fact that liver being the center and target for metabolism may concentrate heavy metals. The high accumulation of Zn in the kidney could be based on specific metabolism process and co-enzyme catalyzed reactions involving Zn taking place in the kidney.

In present study, Cadmium (Cd) concentration was below detectable level in all the organs except liver (0.002 ppm). The cadmium concentration reported in study within permissible limit in liver where as cadmium is Below detectable level in kidney, muscle and gill. Ashraf (2005) reported concentration of 0.41 ppm in the kidney of *Epinephelus microdon* from Arabian Gulf. Nickel (Ni) and Manganese (Mn) concentrations was observed below detectable level in all the organs. Observed concentration of Cobalt (Co) in different body organs was from 0.001 to 0.002 ppm, it was high in the muscle (0.002 ppm) and low (0.001 ppm) in gill, liver and in kidney.

The high metal concentration in fish was mostly found in liver and it was followed by Kidney, gonad, gill and muscle. Liver, known to have high metabolic activities has been widely recognized as valuable indicator of pollution. (Hansen et al., 1982)

In the present study, the concentration of Cu, Fe, Zn, Cd, Ni, Co and Mn were within acceptable limits by international standards (FAO, 1992 and FAO / WHO, 1983). Farombi, *et. al.*, (2007) reported the accumulation levels of Zn, Cu, Cd, AS and Pb in the kidney, liver, gills and heart of African cat fish (*Clarias gariepinus*). The accumulation trend of the metals in organs as: Gills- Zn > Cu > Pb > Cd > As; Kidney- Zn > Cu > Pb > As > Cd; Liver- Zn > Cu > Pb > As > Cd. The order of concentration of metals in the organs as: Zinc - Gills > Liver > Kidney; Copper – Kidney > Liver > Gills; Cadmium - Liver > Gills > Kidney. The levels of heavy metal ranged between 0.69 – 19.05 ppm in kidneys, 2.10 – 19.75 ppm in liver and 1.95 – 20.35 ppm in gills.

The gills are in direct contact with contaminated water and have thinnest epithelium of all the organs and metals can penetrate through the thin epithelial cells (Bebianno, *et. al.*, 2004).

Reddy, *et. al.*, (2007) reported the higher concentration Fe followed by Zn and Mn in some commercial fishes. The accumulation order of heavy metals in fish was as Fe > Zn > Mn > Cu > As > Pb > Hg > Cr > Co > Cd.

Metal concentrations were always lowest in the muscle and highest in the gill and liver. This is due to their physiological roles in fish metabolism. It has been shown that target tissues of heavy metals are metabolically active ones, like liver, kidney and gill. Therefore, metal accumulation in these tissues occur higher level compared to some other tissues like muscle, where metabolic activities is comparatively low (Heath, 1987; Langston, 1990; Serra, *et. al.*, 1993; Roesijadi and Robinson, 1994; Canli, *et. al.*, 1998).

Discharge of untreated industrial effluent into aquatic ecosystem seriously affects the aquatic biota and their production. Anithkumar and Sreeram (1996) have studied the effect of water pollution on the biochemical parameters of selected tissues of *Channa striatus*. Carbohydrates, proteins and lipids are the major biochemical components which act as source of energy for various physiological functions in the body. Many workers have reported the changes in these parameters due to industrial pollution stress. Muley, *et. al.*, (2007) reported that, the industrial effluents from tannery, electroplating and textile mills caused marked depletion in biochemical composition in various tissues of fish *Labio rohita* after acute exposure.

In present investigation, alterations in glycogen, protein and lipid contents of various organs was observed after chronic exposure of industrial effluents on the estuarine catfish species *Mystus gulio* (Ham.)

In fish glycogen, protein and lipid acts as source of energy but among them glycogen is the most prime source of energy for carrying out various activities. The glycogen is one of the cheapest sources of energy in animal food and it plays major role in metabolism. In the control group the content of glycogen in different body parts were in the order of liver > muscle > gill > kidney. In the liver Maximum (7.69 ± 0.30 mg / 100 mg) glycogen content was recorded. The glycogen level in the Kidney was minimum (4.54 ± 0.41 mg / 100 mg).

Under the toxic influence of industrial effluent at $1/10^{th}$ of LC_{50}, concentration, the glycogen was significantly decreased in all the organs like liver, muscle, kidney and gill. They were in order of liver > muscle > kidney > gill. The maximum glycogen content was recorded in liver (3.41 ± 0.25 mg / 100 mg, $P < 0.01$), followed by muscle (3.34 ± 0.48 mg / 100 mg, $P < 0.01$), kidney (2.76 ± 0.27 mg / 100 mg, $P < 0.01$), and gill (1.41 ± 0.18 mg / 100 mg, $P < 0.01$).

Under the toxic influence of industrial effluent at the$1/20^{th}$ of LC_{50} concentration, of the industrial effluent the glycogen content was significantly decreased in the liver, muscle, kidney and gill. They were in order of liver > muscle > kidney > gill. In the liver maximum glycogen content was recorded (5.05 ± 0.49 mg / 100 mg, $P < 0.001$), followed by muscle (4.04 ± 0.91 mg / 100 mg, $P < 0.01$), kidney (3.04 ± 0.07 mg / 100 mg, $P < 0.01$), and gill (2.13 ± 0.11 mg / 100 mg, $P < 0.01$).

In present study, significant decline in glycogen content of all the target organs of experimental fish. It was observed that, there was significant decrease in the glycogen level of experimental group of fishes exposed to the industrial effluents for $1/10^{th}$ of LC_{50} and $1/20^{th}$ of LC_{50} concentration of industrial effluent was noticed. Such significant decline in glycogen may be due to its use as the principle and immediate energy precursor in fish under stress condition. Umminger (1970) suggested that significant decrease in glycogen content in the liver of hill fish *Fundulus heterclitus* indicated the excess utilization of the reserve glycogen to withstand heavy metal toxic stress due to industrial discharge. Similar observations were made by Amutha, *et. al.*, (2002), when the tissues like gill, liver and muscle of fresh water teleost fish *Oreochromis mossambicus* was exposed to dairy effluent. Shaffi (1981) reported that, with increasing concentration of mercury, there was decrease in glycogen level in muscle, liver and kidney. Awari and Gaikwad (1991) reported significant reduction of glycogen content in the liver of *Ambassis ranga* after exposure to Cadmium chloride.

Depletion of total glycogen under pollutant stress has been reported earlier by Bretaud, *et. al.,* (2002) and Naidu *et. al.,* (1984) in liver; Jagdeesh, *et. al.,* (1989) in liver, muscle, and kidney; Arun, *et. al.,* (2000) in gill. Stress response magnitude was dose dependant (Martinez, 2004).

Protein plays an important role in movement, growth, spawning, and metabolic activities of body. Alteration in protein contents in various species were well documented by several workers. Significant decrease in liver protein has been reported in carp exposed to lead (Narbonne, 1973) and juvenile coho salmon exposed to bleached kraft pulp mill effluent (Mcleay and Brown, 1974).Kulkarni and Dharwadkar (1998) reported the effect of dairy effluent on protein content of fish *Hypophthalmichthys molitrix*, in which there was significant decrease in total protein content in fish. Baruah (2004) has studied the effect of paper mill effluent on muscle protein of fish *Heteropneustes fossillis* and showed decline in protein concentration in the early exposed period of 30 days.

Achyutha Devi, and Piska, (2006) reported that, maximum amount of protein declined in muscle followed by kidney, liver, brain and gills as impact of fluoride toxicity. Mercury, copper and cadmium induced changes in the total proteins level in muscle tissue of an edible estuarine fish *Boleophthalmus dussumieri* reported by Kapila and Ragothaman, (1999). Under mercury stress similar results were shown by Suresh, *et. al.,* (1991) in fish *Cyprinus carpio*. The magnitude of these changes increases with period of exposure.

In the control group the content of protein in different body parts were in the order of muscle > liver > kidney > gill. The maximum protein content was recorded in the muscle (26.98 ± 0.47 mg / 100 mg), followed by liver (15.06 ± 0.13 mg / 100 mg), kidney (12.35 ± 0.32 mg / 100 mg), while it was the minimum in the gill (10.50 ± 0.51 mg / 100 mg).

In present study, protein level was significantly decreased in almost all the body tissues of the exposed fishes at the1/10th of LC $_{50}$ concentration to the industrial effluent. They were in order of muscle > gill > kidney > liver. In the muscle maximum protein content was recorded (13.42 ± 0.54 mg / 100 mg, P < 0.001), followed by gill (8.87 ± 0.26 mg / 100 mg, P < 0.01), kidney (5.10 ± 0.36 mg / 100 mg, P < 0.001), and liver (3.40 ± 0.29 mg / 100 mg, P < 0.001).

Protein content was also decreased in the experimental group of fishes when exposed to the 1/20th of LC_{50} concentration of industrial effluent. There was significant decrease in the protein content of all body tissues. The decrease was in the order of muscle > gill > kidney > liver. In the muscle maximum protein content was recorded (16.17 ± 0.32 mg / 100 mg, P < 0.001), followed by gill (9.50 ± 0.11 mg / 100 mg, P < 0.05), kidney (7.58 ± 0.13 mg / 100 mg, P < 0.001), and liver (5.46 ± 0.59 mg / 100 mg, P < 0.001).

In animals, lipid act as a reserved depot of energy, from which the energy is taken when needed. Lipid utilization is for one or some of the functions like during maturation of gametes, drastic environmental conditions, starvation, pollution stress etc. Such role of lipid metabolism in body maintenance under industrial pollution stress can be seen in present study. Katti and Sathyanesan (1983) reported the decrease level in fresh water fish *Clarius batrachus* under the stress of lead nitrate. The significant decrease in lipid occurs because of rapid utilization of lipid to meet subsequently increased demand, created by water pollutants (Rae and Rao, 1981; Kulkarni and Dharwadkar, 1998; Shanthi and Dhanlakhmi, 2006).

In the control group the content lipid in different body parts were in the order of liver > gill > kidney > muscle. The maximum lipid content was recorded in the liver (16.59 ± 0.53 mg / 100 mg), followed by gill (11.19 ± 0.33 mg / 100 mg), kidney (10.69 ± 0.67 mg / 100 mg), and muscle (3.54 ± 0.30 mg / 100 mg).

In the present study, the lipid content was considerably decreased due to exposure of fish 1/10th of LC $_{50}$ concentration. There were non significant depletion in the lipid content of liver and muscle. Decline in the lipid content was in the order of liver > kidney > gill > muscle. The maximum depletion in lipid content was recorded in liver (4.17 ±

0.97 mg / 100 mg, NS), followed by kidney (2.79 ± 0.80 mg / 100 mg, $P < 0.05$), gill (2.67 ± 0.30 mg / 100 mg, $P < 0.001$), and muscle (1.09 ± 0.41 mg / 100 mg, NS).

The lipid content of target tissues gets influenced by toxic nature of industrial effluent $1/20^{th}$ of LC_{50} concentration. As compared to control, lipid was significantly decreased in all the organs like liver, muscle, kidney and gill. It was in the order of liver, kidney, gill and muscle. Maximum decline in lipid content was recorded (6.36 ± 1.17 mg / 100 mg, $P < 0.01$), followed by kidney (5.16 ± 0.74 mg / 100 mg, $P < 0.01$), gill (4.25 ± 0.25 mg / 100 mg, $P < 0.001$) and muscle (1.93 ± 0.21 mg / 100 mg, $P < 0.01$) for the $1/20^{th}$ of LC_{50} concentration.

RECOMMENDATIONS

In order to combat situation the government authorities should plan and implement certain remedial measures.

1. A very good understanding of estuarine processes and its properties.
2. Integrated development plans for limiting the discharge into the estuarine ecosystem.
3. Setting up of an estuarine monitoring centers and institutions to assess the pollution threats and inform the users and the managers.
4. Enacting strict regulatory act with regard to dumping of solid and liquid wastes into estuarine areas.
5. Technology improvement for waste water treatment.
6. Creation of awareness about the importance for estuarine environment among the estuarine users.
7. Protection of existing mangroves is essential.
8. Mangroves plantation programs should be conducted and implemented effectively to minimize load of pollutants and to offer feeding and breeding grounds to the estuarine biota.