CHAPTER – I
INTRODUCTION

Aquatic ecosystems are very vulnerable to water pollution. Most of the Coastal water bodies all over the world are getting polluted thus decreasing the suitability of production. Population growth and result acceleration of domestic municipal, industrial, agricultural and aquaculture activities are the primary causes of anthropogenic pollution of the coastal marine environment. The distribution of metals within the aquatic environment is governed by complex processes of material exchange affected by various natural and anthropogenic activities (Leivouri, 1998; Ip et al., 2007). Since heavy metals are toxic, persistent and non-degradable in the environment, the contamination of sediments by these elements represent greatest ecological risk to coastal marine ecosystem (Gracia et al., 2008).

Fishing sector playing a significant role in satisfying not only nutritional need of mankind throughout the world, but also contributes much to development through better income, employment opportunities and increasing returns from resources use. There are a number of poor people in the world who rely on fisheries for food and income. More importantly, for many fish happens to be their primary sources of protein. Globally fish provides about 16% of the animal protein consume by humans. Fish is also available sources of minerals and essential fatty acids to human beings (Khan and Abidi, 2007). Fish has been repeatedly described as healthy promoting food category (Mozaffarian & Rimm, 2006; Sidhu, 2003). The average global per-capital annual consumption of fish has also increased from about 12 kg in 1973 to nearly 16 kg in 1997 (Delgado et al., 2003). These factors have been responsible for an increase in total consumption of food fish from 40 MMT, in 1970 to 86 MMT in 2000 and expected 140 MMT by 2025 (FAO, 2009). Most natural fish stocks are unable to sustain even their current productivity in the face of heavy fishing pressure and declining environment quality.
Estuaries are one of the important environments of coastal zones and they constitute transition zones where freshwater entering into seawater. Biological connectivity between sub-tidal and intertidal habitat are formed by estuaries, which are dense with mangrove forest and act as nursery grounds for the most of the fish populations. The mangrove swamps offering suitable food supply, shelter and ecophysiological conditions for larvae and juvenile fish population development (Blaber and Blaber, 1980). It is well documented that many population of the coastal fish depend on such critical areas, at least during part of their life cycle (McHugh, 1985; Yánéz-Arancibia and Sánchez-Gill, 1988). The economic values of the estuarine ecosystem far outweighs, if relative global area: in a view of economic value of the world ecosystem (Costanza et al., 1997); estuaries had highest total value for hectare. The fishes and many of the invertebrates of estuaries and have formed the basis of the development of great variety of fishes (Blaber, 2000a).

Accelerated loss of coastal and marine organisms over the last few decades has been of great concern. Environmental changes, over-exploitation and habitat loss are among the major cause of species loss that, according to certain estimates, is of the order of a species per day (Venkataraman and Wafer, 2005). Anthropogenic activities as well as ecological processes contribute to the fish states of mangrove swamps. It is also strongly affected by socioeconomic factors such as land policies, population migration, urbanization, resources availability, other commercial activities and market for the resources. Thus, studies on status of mangrove swamps require an integrated interdisciplinary approaches as an alterations or disturbances of the mangrove swamps can have an adverse impact on the environmental and fishery potential.
1.1 Significance of fisheries

Fisheries play an important role in the world food economy and its source of employment opportunities of many countries. The fishery sector has been globally recognized as an important source for providing the growing protein requirements of ever increasing human populations. Although other reason such as sport or recreational fishing, industry oriented fishing, obtaining or ornamental fish, fish oils also encourage fishery. It is potential answer for the growing problems of global dietary animal shortages. Fish are able to convert the feed, they consume into flesh about two times more efficiently than chicken and five to ten times more efficiently than cattle (Khan and Abidi, 2007).

Fish are an important part of a health diet since they are considered to be an excellent source of high value protein essential nutrients. Fish are low in saturated fat and contain poly saturated fatty acids such as omega-3, where a well balanced diet can contribute to reduced heart disease and promotes the proper growth and development in fetuses and children (Buger and Gochteld, 2004; Hunter 1998). During the last decade, the importance of omega-3 fatty acids in the diet has been recognized. Such acids are believed to play an important role in protecting against heart disease by various ways including preventing blood cells from clothing and adhering to artery walls of decreasing triglycerides and low density lipoproteins (Connor, 2000; Sidhu, 2003) in addition to having anti-arrhythmic effects (De Caterina et al., 2003). Fish consumption has been associated with improved pregnancy outcomes, including fever pattern and low birth-weight deliveries (Olsen and Secher, 2002) attributed in part, at least, to n-3 fatty acids (Allen and Harris, 2001). Fish are also thought to reduce the risk of stroke caused by blood clots (Kris-Etherton et al., 2002) and to play a role in decreasing inflammation while benefiting people with autoimmune disease (Simopoulos, 2002).
1.2 Coastal Zones

There are several definitions for the coastal zones, however, the following is common and accepted by world scientific community, is “The land and water extending inland for one kilometer from high water mark on the offshore and extending seaward to the 30 meters depth contour line, and also including the water beds and banks of all rivers estuaries inlets, creeks, bays or lakes subject to the ebb and flow of the tide” (Beer, 1997). Accordingly, coastal zone extends inland as far as the tide affects the shore. Estuarine and deltaic river mouths can be brought of has comprising coastal waters. The line which separates the marine waters from the terrestrial domain is called the shore line, which constitutes a very marked physical barrier for living organisms on the planet Earth.

Most of the coastal regions in the world are characterized by ecological sensitive fragile ecosystems essentially because they represent the interface between land and the sea. These coastal areas are being subjected to high human pressure, has mass movement of people has been observed from the hinterlands the coastal areas during late 20th and 21st centuries. The world population, around 40 percent is residing within the 100 km of the coastal line (Noronha, 2003).

India has an average of 3,28,782 km$^2$, located in the northern hemisphere between $8^0$ 4' and $37^o$ 6' North latitude and $67^o$ 7' and $97^o$ 25' East longitude. The country is characterized by a variety of physical features ecological and climatic conditions ranging from dry to wet and hot cool with different combinations of rainfall temperature, humidity physiography and biotic stresses. Physiographically, it is divided in to four main regions: The Northern mountains the great plains, the peninsular plateaus and the sea coast and island (Kumar, 1995). The main land coast line admeasures to around 6100 km length, bounded by the Arabian Sea to west, the Bay of Bengal to the east and the Indian Ocean to the south. Deltas and
Estuaries are quite significant among the features of Indian shore. However, deltaic region are more predominant to the eastern coast and estuaries largely occur on the western shore, due to the gradual slope towards east and steep topography to the west respectively (Ahmad, 1972a).

**1.3 The Coastal regulation zone**

The Ministry of Environment and Forest (MoEF), Central Government of India, is constantly instrumental for strengthening existing policies for protecting and improving the quality of the coastal environment. The legal system of coastal zone management in India comes into force in 1991 (Anon, 1999). The Coastal Regulatory Zone (CRZ) notification, under the environment Act, is one of the major norms limiting the activities in the coastal zone. It includes various laws for regulation of anthropogenic interferences by permitting environmental responsive developments. Coastal stretches of seas, bays, estuaries, creeks, backwaters and rivers, which are influenced by tidal action (in landward side) up to 500 m from the high tide line (HTL) and the land between this HLT and LTL (low tide line) is declared CRZ.

**1.4 Estuaries**

Estuarine environments are vital habitats for many species of fish, crustaceans, and molluscs serving as spawning grounds, nurseries, and feeding grounds and also important for early growth. The definition of estuary coined by Day (1981), is widely accepted by biologists, which reads as “An estuary is partially enclosed coastal body of water is either permanently or periodically open to the sea and within which there is a measureable variation of salinity due to the mixture of seawater with freshwater derived from land drainage”. Tropical estuaries grade into subtropical systems beyond the tropics of Cancer and Capricorn, when seasonal water temperature difference become more marked. The differences between summer and winter conditions were separate the tropical and subtropical estuaries.
Estuaries from the tropics represent one of the most exploited ecosystems in the world (Blaber, 2000b).

Estuaries have huge ecological value and have frequently been referred to as fish nursery areas (Franco-Gordo et al., 2003; Berasategui et al., 2004) and sustaining many marine fish species mainly represented by larvae and juveniles (Duffy-Anderson et al., 2003, Castro et al., 2005). Adults and larvae of fish occurrence and distribution in an estuary vary according to environmental changes like: precipitation regime, estuary morphology that determines the intensity and distance of salt wedge inversion, tidal dynamics, current velocity and availability of food resources (Camargo and Isaac, 2003; Re, 2005). There are rich in biodiversity and many have the highest economic values per hectare relative to any other aquatic environment (Costanza et al., 1997). Therefore, conservation and protection these water bodies should be on top priority in order to maintain their viability for biodiversity and fisheries production.

1.5 Metals in the marine environment

Various contaminants released into the seas may significantly affect marine ecology, and in extreme cases, may lead to the destruction of whole ecosystem. The contaminants major concern in this area are agriculture, sewage, nutrients, metallic compounds persistent organic pollutants, petroleum hydrocarbons and other type of aqua effluents. Many contaminants such as heavy metal though occur at extremely low concentrations in sea water, are accumulated by marine organisms and concentrations in their body tissue can be hundreds of times greater than the levels of sea water Unlu and Gumgum (1993) reported that levels of metals in upper members of the web like fish can reach level many times higher than those found in aquatic environment or in sediment. Fish accumulate different levels of metals depending on many factors such as physiological needs, feeding habits and genetic composition, sea of the fish species,
and the biochemical significant role of each metal (Huang, 2003; Kamaruzzaman et al., 2010).

The outbreak of hitherto disease unknown neurological illness among the inhabitants living around Minamata bay, Japan was reported in 1953. The victims suffered from a weakening of muscles, loss of vision, impairment of cerebral function and eventual paralysis and death. After intensive investigations it was found that in 1959 the cause of the disease was due to the consumption of fish and other food stuffs contaminated with methyl-Hg, the source of which was traced to the effluent of chemical industry manufacturing plastics. This disease become known as Minamata disease.

Contamination of aquatic environment by Cd is less widespread than by Hg. During 1947 an unusual and painful disease, subsequently became known as “Itai-Itai,” was reported among the villages on the bank of the Jintisu River in Japan. Contamination of river water by Cd was found to be the culprit source of Cd was traced to a Zn mine situated some 50 km upstream form affected villages. It is estimated that at least 100 deaths occurred due to disease until, 1965. An interesting episode of mass mortality of fish resulting from a poisoning occurred off the coastal of Holland (Wittaman, 1979).

Nriagu and Pacyna (1988) have assessed the world wide contaminant of air, water and soil by trace metals, and analyzed the different sources where trace metal impact has resulted in the environmental change.

The inventories presented clearly show that mankind has become the most important part in the global biogeochemical cycling of trace metals. A comparison of the Mechian values of worldwide emission of trace metal from natural and anthropogenic sources. Nriagu (1989) reported that the industrial emissions of Pb, Cd and Zn exceed the flux from natural sources by factors of 18, 5, and 3 respectively. Industrial discharges are apparently exerting a profound
influence on the atmosphere cycles of these toxic metals. The influence of increased metal levels due to human activities is found in all parts of the hydrological cycle and the atmosphere plays a unique role as a carrier. Metals are emitted to the atmosphere from anthropogenic, terrestrial and aquatic sources, which, through the atmosphere, are distributed among the components of the ecosystem, and are integral to the biogeochemical cycling of these elements. Because of the dynamic nature of the atmosphere, metal can be carried for long distance and be deposited in areas remote from their initial sources.

1.5.1 Metals in marine biota

Essential metals such as Zn, Cu and Iron have important biochemical functions in the organisms and form either an electron donor system of function as ligands in complex enzymatic compounds (Forstner, 1979). In natural marine environment their enrichment in organisms does not exceed the level to interfere with the enzyme system functioning through their concentrations in organisms are generally higher than in sea water. However, if the ambient water or toad contains high concentration of these metals the homeostatic mechanisms to function and essential trace metals act in an either acutely or chronically toxic manner. Simkiss and Taylor (1989) have discussed the path ways of metal accumulation of aquatic organisms and suggested possible types of uptake. The most common is by a passive process of transfer from sea water down a concentration gradient in to the tissues. In some cases, uptake may also occur through ion pumps because of energy dependency. For many metals including Cd, Cu, and Zn, the free a metal ion is the most bio-available form of the elements (Goldberg et al., 1976a, 1976b).

Variations in concentration of trace metals between species particularly in heterotrophs can be due to tropic level relationship (FAO, 1976). Though magnification of trace metals through the food web is important, there several other causes affecting the transfer of
trace metals in marine organisms. There is also evidence of seasonal variations in the trace metal content within species (FAO, 1976). The biological uptake retention and translocation of trace metals in marine biota are related to chemical changes in storage tissues within the organisms (FAO, 1976).

1.5.2 Metal in marine sediment

Metals in marine sediments can originate from several sources. Inshore and coastal area are major source of metal is lithogenous associated with weathering products from the source of rocks. Hydrogenous formations that include precipitation products and metal absorbed on particles formed due to physico-chemical changes in water also contributes to the metal burden in marine sediment (Riley and Chester, 1971). Anthropogenically introduced metals are ultimately transferred to the bed sediments (Simeonov et al., 2000; Marchand et al., 2006). The sediment analysis do not represent the extent of toxicity, they are useful to assess the burden of anthropogenic component over and above the lithogenic background and also in some instances, trace the sources of pollution long after input has taken place (Fukue et al., 1999; Buccolieri et al., 2006).

Rate of urbanization and industrialization increased after World War II and several industries including a Pb smelter released their effluent in the Bay (Hornberger et al., 1999). In 1980, approximately 100 T of trace metal (As, Cd, Cr, Cu, Pb, Hg, Ni, Zn) were discharge to the south San Francisco bay from 24 wastewater treatment plants. (Hornberger et al., 1999). Mass balance calculations indicated that those excesses were primarily due to anthropogenic inputs and digenetic remobilization from benthic sediments (Flegal and wihelmy, 1991). The metal pollution assessment through sediment analysis are available in the literature (Simeonov et al., 2000, Buccolieri et al., 2006 and Marchand et al., 2006).
1.5.3 Metals in organisms

The investigations on the concentration of metals in marine organisms of the India are limited to only a few are: (Zingde et al., 1976; 1979; Patel et al., 1985; Srinivas and Mahajan 1987; Abhay Kumar Singh, 1999; SenGupta and Qasim, 2001; Mishra et al., 2007; Krishna et al., 2014). The past and recent data indicate to that general absence of bioaccumulation in the organisms studied except localize areas receiving anthropogenic metals. The contamination of the aquatic environment and also organisms in the east coast of India. That has been accelerated developments in terms of industries and port activities recent years.

1.6 Selection of elements and their toxicity

Metals as Cd and Pb are non essential metals and their toxic effects on human health is well known. While metals as Zn, Iron and Cu are essential metals, the toxic effect of them on human health begins when they are present in high levels. These elements may be added on the ecosystem through human anthropogenic activities or from natural resources explained previously. Many studies assessed concentration of these heavy metals in various aquatic organisms all over the world. The metal concentrations were determined in fishes (Kavi Raj, 1989; Sultana and Rao, 1998; Saha 2006; Lata, 2013) and in several cases concentrations of some metals were exceeding the permissible limited allowed by international organization such as WHO and FAO (Krishna et al., 2014).

1.6.1 Selected elements and their toxicity

1.6.1.1 Cadmium

Cadmium is a metal from group II B that has an atomic weight of 112.41 with specific gravity of 8.65; the ionic form of cadminium (Cd\(^{2+}\)) is usually combined with ionic forms of oxygen cadmiumoxide, CdO): Chlorine (Cadmium Chloride (Cdcl\(_2\)) or sulfur Cadmium sulphate, (CdSO\(_4\)) cd is a natural element in the earth crust. It is
usually found as a mineral with other elements. All soils and rocks including coal and mineral fertilizers have some Cd in them. In industry and consumer products, it is used for batteries (Ni/Cd) batteries of mobile Phones), Pigments, metal coatings and plastics. It is also constituent in many other things such as alloys. Cd enters air from mining, industry and burning coal and household waste. Its particles can travel long distance in air before falling to ground or water (Singh, 2005).

Cadmium is widely distributed at low levels in the environment and is a non-essential element for human, animals and plants. Toxicity symptoms included by Cd include gastrointestinal that intoxication with Cd in pregnant woman has been related to reduced pregnancy length and newborn weight and, recently to discover of the endocrine and /or immune system (Schoetens, et al., 2006). The carcinogenic risk from cadmium exposure, IARC (1993) concluded that there was sufficient evidence to classify cadmium and cadmium compounds as human carcinogens (Group–I). This assessment was, to a great extent on the significant relationship between the risk of lung cancer and estimated cumulative exposure to cadmium reported by (Thun et al., 1985) and Stayner et al. (1992) in their analysis of mortality in a cohort of workers from a single cadmium recovery plant in the United States of America.

**Lead:** Lead is a naturally occurring element, it is a member of Group 14 (IV A) of the periodic table, has an atomic weight of 20.72; with specific gravity of 11.34 and exists in three states: Pb (0), the metal; Pb (II); and Pb (IV). Lead is a bluish-gray heavy metal and it is usually found combined with two or more other elements to form lead compounds (Agency for Toxic Substances and Disease Registry, 2007). Lead is found in small amount in the earth’s crust. In can be found in all parts of our environment most of it came from human anthropogenic activities. The principal source of Pb in the marine environment appears to be the exhaust of vehicles run with leaded
fuels that reaches the sea water by a way to be the exhaust of vehicles run with leaded fuels that reaches the sea water by a way of rain and wind blow dust (Castro and Huber, 1997). Lead is found at high concentration in muscles and organs of fish. When accumulates in the human body, it replace calcium in bones. Lead exposure has been mainly related to retardation of neurobehavioral disorder (Lidsky and Schneider, 2003). Data from European Food Safety Authority (EFSA) have related exposure to Cd and Pb to effect like neurotoxicity, nephrotoxicity, carcinogenicity and endocrine and reproductive failure in adults (Herreros et al., 2008). The health hazards of toxicity and disruption of biosynthesis of hemoglobin, rise in blood pressure, damage to kidney brain and nervous system, miscarriage and behavioral disruption of children such as aggression, impulsive behavior and hyperactivity (Jarup 2003 and Durcibe et al., 2007).

**Zinc:** Zinc is naturally present in the environment, rocks, soils water and air. All living organisms during process of evolution have used the Zn available in their environment for vital functions of their metabolism. Hence, Zn is essential and inespeble for all the living organisms in all ecosystems. Further, Zn belongs to group II-B of the periodic table, it has atomic weight 65.38, and density 7.13 (Bradi, 2005). The most common minerals of Zinc are Zinc sulphate (Zns), Zincite (Zno) and smith-sonite (Znco3) (Momtaz, 2002). The chronic (sub-lethal) toxicity test can be performed in order to determine the organisms response to less severe condition than present in acute effect and usually after a long term. Low levels of toxicants in water do not produce mortality in a population of organisms but impair of inhibit reproduction, growth or behavios at chronic toxicity levels (Simsek, 1996).

Zinc is an essential trace element for all living organisms. As a constituent of more than 200 metallo-enzymes and metallic compounds, Zn assures stability of biological structure suctions membranes and ribosome. Excessive Zinc concentrations can have
severe impact upon the survival and growth of aquatic organisms (Eisler, 1993; Vallee, 1959). The dissolved Zinc in sea water is complexed by chloride and hydroxide with about 47% present as the free $\text{Zn}^{2+}$ ions (Zirino and Yamamoto, 1972). In natural waters, dissolved Zn speciate into the toxic aquo ion ($\text{Zn} (\text{H}_2\text{O})_6^{2+}$). Aquo ions and other toxic species are most harmful to aquatic life under conditions of low $p^\text{H}$, low alkalinity, low dissolved oxygen and elevated temperature.

**Copper:** Copper belongs to group I–B of the periodic table, it has an atomic weight of 63.55 with a specific gravity of 8.96 with oxidation state of +2, +1. The important ores of cu are chalcocite (Cu FeS_2), cuprite (Cu_2O) and Malachite (Cu Co_3. Cu (OH)_2). Copper is widely used for wire production and in the electrical industry. Its main alloys are brass (with Zinc) and bronze (with tin). Other applications are kitchen ware, water delivery systems and copper fertilizers (Bradi, 2005). Copper is considered as an essential constituent of metalloenzymes of living organisms and is required in hemoglobin synthesis and in catalysis of metabolic reactions (Dural et al., 2007). It plays a crucial role in many biological enzyme systems that catalyze oxidation/reduction reactions. However, it present at relative high concentration in the environment toxicity to aquatic organisms may occur. Copper under ionic forms $\text{Cu}^{2+}$, $\text{Cu}_2 \text{OH}^+$ and $\text{CuOH}^+$ is too toxic to fish (Moore, 1991). Copper levels lead to an increase in the rate of free radical formation (Gwozdzinski, 1995), teratogenicity (Stouthant et al., 1996), and chromosomal aberrations (Bhunya and Pati, 1987; Fahmy, 2000).

**Nickel:** Nickel is a silvery white, hard and malleable metal. It belongs to the iron cobalt group of periodic table; Ni has atomic weight of 58.71, with specific gravity of 8.9. It is very abundant element. It is found in all soils and is emitted from volcanoes. It is normally occurs in oxidation states O and II. Nickel is used as an alloy in the steel industry, electroplating Ni/Cd batteries, welding pigments for paints
and ceramics, surgical and dental prosthesis, molds for ceramic and glass containers, computer components and catalysts (Bradi, 2005).

Nickel is an essential food stuff in small quantity (Lenntech, 2004). Humans may be exposed to nickel by breathing air, drinking water, eating food or smoking cigarettes. Skin contact with nickel contaminated soil or water may also result in nickel exposure. In small quantity, nickel is essential but when maximum tolerable amounts is exceed, it can be dangerous to human health. Health hazardous involved with high Nickel up take are sickness and dizziness, birthdefects, asthma, chronic bronchitis, respiratory failure, allergic reactions, heart disorders and cancer of nose, larynx and lungs (Lenntech, 2004).

**Aim and scope of the present study:** The great concentration of monitoring studies conducted by many countries have been concerned with obtaining information on heavy metals concentrations in water, sediment and biota, of their respective coastal regions with the emphasis on the later being often to allay public health concerns. Fishes are considered excellent indicator organisms because of their ability in concentrating metals among the pollutants there has been a depth in studies on documenting the seasonal variation of heavy metals in water, sediment and biota in the coastal waters of India, besides measuring concentrations of these metals in aquatic organisms and its hosts environment. There is need to study effects of concentrated metals on organisms and on ecosystem. This will require careful evaluation of impact of metals on various tropic levels in marine ecosystem and movement of metals through food web. Sediments being ultimate repository of contaminants, this can act as a source of contaminants in fauna for accumulation and finally find this way into seafood consumers. The present study is mainly based on the heavy metal contamination in marine environment, its accumulation in sediment, fishes and to observe the metal toxicity flow through benthic food chain (sediment-crustacean-small fishes –
food fishes. The metal discussed in the study include Lead (Pb), Cadmium (Cd), Copper (Cu), Zinc (Zn) and Nickel (Ni). These metals have been selected due to their diverse application in a majority of the commodities produced by the modern society, their toxic effect on living organisms and their levels are easily measurable in samples. The seasonal changes in the concentration of these metals along with the coast with special emphasis on the waters of Machilipatnam were also studied as a part of this study. In the present study, an attempt was made to determine the distribution of heavy metals in the tissues of two species of economically important fishes from the Machilipatnam coast and from the east coast of India.

**Objectives of the study**

- To study the significance of fisheries, metals in the marine environment, metals in marine biota, selection of metals and their toxicity.

- To review the present status, metal pollution status, previous status of metal Pollution in water, sediment and organisms.

- To study the food and feeding habits of selected food fishes in the Machilipatnam coast.

- To study physico-chemical parameters of water in the Machilipatnam Coast.

- To study the heavy metal concentration of selected heavy metals Pb, Cd, Cu, Zn and Ni in the water, sediment and selected fish tissues of *Upeneus sulphureus* and *Terapon jarbua*.

- To observe the THQ values and health risk assessment of the fish Consumers of Machilipatnam area.