FINAL PROJECT REPORT

1. Project No. #: 50022801

2. Project Title: **Study of Heavy Metal Pollution Level and Impact on the Fauna and Flora Of the Karachi and Gwadar Coast.**

3. Project Start Date: October 2001

4. **Project End Date**: September 2002

5. Report Prepared by: Monawwar Saleem

7. Introduction:

Karachi is located on the northern border of the Arabian Sea and its population is over thirteen million. Karachi coastal area receives 472,000m3 domestic and industrial wastewater primarily through Lyari and Malir River and from streams and drainages (KDA master plan[1], 1990-2000). This water reaches Karachi coastal area via Karachi Harbour and Gizri creek. Industrial waste discharge originating form the industries located at SITE (Sindh Industrial Trading Estate), LITE (Landhi Industrial Trading Estate), KIA (Korangi Industrial Area) that also add their effluent to Karachi coastal area. The two existing treatment plants located at Malir and Lyari Rivers treat approximately 20-25% of the total waste. Karachi coastal area is badly affected by industrial and untreated sewage of Karachi Harbour and Gizri and Korangi creek. According to Beg[2] (1975) Karachi Harbour receives a variety of chemicals such as calcium carbonate (115.74 metric tons/day) total dissolved solids (317 metric tons/day) iron oxide (5.14 metric tons/day). Due to the tidal flushing of wastes in the Karachi Harbour and Gizri and Korangi creek the highly toxic wastes make their way in to the coastal waters of Karachi resulting the increasing levels of pollution. Preliminary survey of Karachi Harbour seawater reveals that it contains high concentration of nutrients downstream of Lyari River Monawwar[3] (1995). The tides of the Karachi Harbour are semi diurnal type Quraishee[4] (1975). The effluents received by the Karachi Harbour through Lyari River and the adjoining areas are not completely flushed out in to the open sea during tidal cycle. Therefore poor circulation condition creates production of hydrogen sulfide that produces a stress on the marine life. Tidal flats of the Sandspit and Channa creek in the Karachi Harbour area have flourishing vegetation of mangrove. The most part of the central area of Karachi Harbour and some area of Korangi creek are devoid of any benthic life in the sediments. The bottom sediments are black in colour with presence of hydrogen sulfide. The fauna and flora of this area are severe stress from the industrial and domestic pollution (Ahmed[5], 1979).

The city of Gwadar is located at the extreme northern border of the Arabian Sea, some ~450 km west of Karachi. The population of Gwadar is over 120,000. More than 50% of the population is engaged in fishing activity. The fishermen's boats occupy a very large stretch of the East Bay where fish landing and boat building and repairs take place. About 400 boats (mostly small) are busy in fishing in the territorial waters. According to Rabbani[6] (1989) the area is highly productive and red tide blooms have been observed in the winter monsoon period. Gwadar city has no proper drainage system; the liquid waste is dumped septic tank (underground). According to Memon[7] (1995), heavy minerals are found in the range of 1-.15%. High concentrations of heavy metal in water and sediment have also been observed in Karachi Harbour and in the sediment of Gwadar East Bay (Monawwar[8], 1999). Continued disposal of the industrial and domestic waste in to Arabian Sea will cause fish kill and reduction in the valuable export of shrimps as well as the reduction of marine life in the coastal waters. Some work has been done regarding the heavy metal concentration in the fish and shellfish of the Karachi offshore, Korangi creek, and Karachi Harbour (Ashraf[9], 1988; Monawwar[10],,1999)

8. Objectives:

- Estimate the level of heavy metals (Cd, Pb, Ni, Cu, and Hg) in the seawater at hot spot sites of Karachi and Gwadar coast.

- Determine the heavy metal in the marine sediments and biota of Karachi and Gwadar coastal area.
- To determine any heavy metal indicator species of Karachi and Gwadar coastal areas.
- To establish the relationship of heavy metal pollution in marine biota with the environment.

9.Project Achievements (Short and long term):

Result and discussion provide the following useful information: -

- From this project, the data information on heavy metal distribution patterns at selected sites in the seawater, sediments, fauna and flora of Karachi and Gwadar coastal areas has been recorded.
- The project provides a comprehensive baseline data for heavy metals that would be useful for pollution monitoring of the study area in future.
- Data of bioaccumulation obtained from this study will help in determining possible health risks by consumption of seafood from the area.
- The results of this study will also provide a baseline for the assessment of the impact of disposal of industrial and municipal wastes in the entire area of the environment.

10.Constraints & Obstacles encountered:

Time required for the sampling collection and analysis was constraints**.** This was overcome by extending the report period.

11. Action taken to overcome constraints & Obstacles

The WWF-P Scientific Committee was requested to extend the time period, which was granted to me.

12.Target/ Objective not achieved and why?

The target/ Objectives set out in the initial proposal have been achieved.

13. Described the methods developed for the project:

The following protocols were adopted for the collection of samples and data analysis.

13.1 Collection of surface sediment

Seabed sediment samples were collected using Peterson Grab at eight stations in Gwadar East Bay, four stations at Karachi Harbour, three station in Korangi creek area and one each in Gizri Creek, Buleji, Manora (open sea side), (Fig.1-3). A part of the sample from middle of the grab was retained for analysis. Soon after the collection of samples, the sediment samples were kept in polyethylene wide neck bottles (Pre-washed with 10% HC1 acid) and stored in iceboxes and refrigerator until analysis. The sediment samples were collected from Karachi coast in January 2002 to July 2002. The sampling from Gwadar was done in the middle of July 2002.

13.2 Collection of seawater samples

Seawater samples for dissolved heavy metals were collected using Niskin bottles / plastic Bucket (pre-washed with distilled water). These seawater samples were collected at above station along with the stations. Immediately after the collection of seawater it was filtered through micro glass fiber filter (0.8 µ) paper followed by membrane filter (0.45 µ) under 300 mm Hg pressure acidified with hydrochloric acid to pH-2 and kept in cool place in polyethylene (Nelgin) bottles until analysis. All equipments and filter were of non-metallic materials, carefully acid washed with 10 % hydrochloric acid and rinsed with double distilled water.

13.3 Collection of fish and mussel samples

The fish and shellfish were collected by a trawl net at high tide from the Manora Channel (Karachi Harbour) and in Korangi creek (Fig.1-3). These samples were taken between January and July 2002. Fifteen fishes (Pelagic and benthic) were also collected from Gwadar East Bay during the mid of July 2002. Soon after the collection, the samples were rinsed with distilled water. These samples were identified to the species level and stored in deep freezers until analysis.

Mussels *(Perna viridis)* were collected random by hand picking from each site of Manora channel (Karachi Harbour), Korangi creek and Gwadar East Bay (Near fish harbour) during low tide in January & July 2002. (Fig.1-3). In the laboratory, the samples were cleansed to remove the mud or any attachment and then washed with double distilled water. Tissues (edible portion) from the shells were removed with a plastic knife and kept in pre-cleaned Petri dish. Finally the edible portion samples were dried in the oven at 65°C.

13.4 Collection of seaweeds and mangrove plant leaves

Seaweeds were collected by hand picking from two different sites of Karachi coast, Manora Island (Sea-side) and Buleji during low tide in January 2002; Mangrove leaves were collected at four different sites (Sandpit back water, Karachi Harbour, Kemari back water, Korangi Fish Harbour and Rehri Goth) of the Karachi coast in January 2002. These samples were cleaned and rinsed with double distilled water, and finally dried at room temperature.

13.5 Digestion and analysis of sediment samples

One to four gram of dried sediment sample were added to 3 ml concentrated nitric acid and 9 ml of hydrochloric acid *(Aqua regia)* in pre-washed beaker and digested at room temperature. The sediment samples were then evaporated almost to dryness at moderate temperature 65-70 C° on the hot plate under the clean air-fuming hood. Finally, the samples were diluted up to 25 ml with 2% nitric acid (FAO, 1975)[11]. Heavy metals (Cu, Cr, Ni, & Zn, in the sediment samples were analyzed on Flame Atomic Absorption Spectrophotometer (FAAS) using PERKIN-ELMER Model 3300, Cadmium samples were analyzed on Graphite Furnace Atomic Absorption Spectrophotometer (HGA-600 Perkin-Elmer).

13.6 Extraction of heavy metals and analysis from the seawater samples

300ml to 1000ml samples of seawater was transferred to a pre-washed separating funnel and 1.0 ml of citrate buffer was added. The pH of the samples was adjusted to 4.0 with concentrated hydrochloric acid or purified ammonia. After adjusting the pH, 2 ml of 1.0 % chelating reagent APDC (Ammonium Pyrolline Dithocarbamate) solution was added followed by 20 ml MIBK (Metyl Isobutyl Ketone) The mixture was *kept* for 2 to 3 minutes and they were allowed 15-16 minutes for the separation of phase, subsequent the lower organic layer was drained in 100 ml separating funnel. The procedure was repeated by adding an additional aliquot of 10 ml MIBK to the funnel shaken after 2 to 3 minutes the two extracts were combined and 0.5 ml of nitric acid was added by micropipette mixed for one minute and left for 15 minutes. Subsequently 9.5 ml of double distilled water was added for back extraction (Kremling[12], 1983). After phase separation, the aqueous phase was collected in pre-cleaned Nelgin polyethylene bottle for analysis.

Measurement of heavy metal in seawater was made with Flame AAS / Graphite furnace. Standard operating conditions of the instrument were set during the analysis for Cadmium, nickel, copper and chromium in seawater.

13.7 Digestion and analysis of heavy metal in fish, shellfish, seaweeds, and mangrove leaves

Approximately 1 to 3 gram dry weight of marine organisms (For Fishes edible portion and whole soft tissue of Mussels), seaweed and mangrove plant leaves were mixed separately and to each digestion vessel were added 3 ml of Nitric acid, 9 ml of Hydrochloric acid (Aqua regia) and 5 to 15 ml of Hydrogen peroxide according to the FAO[11] (1975) Manual and were digested at 70-100°C to dryness. After removal from hot plate, the samples were cooled at room temperature, and then added with 25 ml of 2% of nitric acid and kept for two hours. The samples were then filtered by Whatman No.42 filter paper.

For calibration purpose known concentration of each element was added to digest the samples and recoveries were >92% for the known amount of each element. All samples and blanks were analyzed using double beam Atomic Absorption Spectrometer (Perkin-Elmer model 3300). Zinc, copper and chromium were analyzed on flame, while cadmium and nickel on Graphite Furnace (Model HGA-600)

14. Lessons learnt from the project:

The presence of heavy metal pollution in the coastal waters of Karachi is significant as shown in the results and discussion. The heavy metal concentration at Gwadar was however lower. But we must not be complacent. Awareness and the efforts for the containment of heavy metal must continue to be monitored at regular intervals and brought to the notice of the concerned authorities.

14. Result and discussion

14.1 Concentrations and distribution of heavy metals in sea water

The observation of heavy metal concentration levels recorded at four different sites of Karachi coastal area (Karachi harbour, Buleji, Korangi and Gizri creek) and Gwadar East Bay and off-Gwadar East Bay five heavy metals (zinc, copper; cadmium, chromium and nickel) were studied their levels are given in fig.4-fig 6). Generally the concentrations of these metals were found highest in following order; Karachi Harbour> Korangi creek > Gizri creek> Buleji in Karachi coast and in Gwadar East Bay. The high concentration of the heavy metals in seawater in the Karachi Harbour, Korangi and Gizri creek indicates that the area continuously receives industrial and domestic waste of Karachi city, while Buleji is relatively less polluted.

14.1.1 *Nickel*

The concentration of nickel in the Karachi Coast ranges from 0.27 to 0.72 µg/l (Fig.4). Highest concentration of nickel was found in the Karachi Harbour (Mean 0.72µg/l) and lowest in Buleji and Gwadar East Bay 0.27 and 0.42µg/l respectively. High concentration of nickel in Karachi Harbour is due to the waste originating from the electroplating industries at S.I.T.E. Similar trend of nickel distribution was observed by L.Brugman[13] (1998) in northern part of the Baltic near Skagerrak area. Seng[14] (1987) also noticed high concentration of nickel (1.6-1.8 µg/l) in the Juru Estuary due to the industrial activity along the coast (Table-I). At least 40 times lower concentration of nickel was found in our coastal area in comparison with the recommended marine water quality standard for UK for the protection of marine life (Mance, 1984)[15].

14.1.2 *Copper*

The concentration levels of copper in the water samples of Karachi Harbour are found to be highest. Mean value obtained was 2.13µg/l, and low values were found at Buleji and Gwadar East Bay 0.85 0.98µg/l respectively (Fig.4). High concentration in Karachi Harbour can be attributed to the release of copper from the industries and other coastal installations. Comparatively higher concentration of copper in the seawater are reported by Patel[16] (1985) in Bombay harbour, Mart[17] (1985) in Elbe Estuary, Harper[18] (1991) in Severn Estuary, Sengupta[19] (1978) in Goa and Zingde[20] (1987) in Perna River Estuary .On the other hand lower copper concentrations were recorded by Seng[14] (1987) in Juru Estuary, Fowler in Oman coastal water and Valanta[21] (1983) in Wester Shedlt Estuary

(Table-1).

During the present study, a decrease in the concentration of copper was noted from Karachi Harbour towards the open sea. Kremling and Peterson[22] (1984) made similar observation in the Bothnian Bay.

14.1.3 *Zinc*

The concentration level of zinc at the Karachi Coast ranges from 3-24.3µg/l, while in the Gwadar East Bay the concentration ranges between 12-13µg/l (fig.5). The results obtained for zinc in Karachi Harbour are similar to the observations made by Bryan[23] (1976) in Corpus Crusty Harbour in Texas, during the summer when the harbour water stagnates and concentration of zinc was 480µg/l. Wong[24] (1980) also observed high concentration of zinc i.e.38 to 94µg/l in the Tolo Harbour, Hong Kong (Table-1). Accumulation of zinc in seawater in present study shows discharge from the Karachi Harbour and Korangi Creek.

14.1.4 *Cadmium*

Highest mean concentration level of cadmium has been recorded in Karachi Harbour to be 0.485µg/l about half of its concentration is reported in the Korangi creek, while lowest was recorded in Buleji (0.063µg/l) table-5. According to a published report Industrial and domestic waste is considered to be the main source of cadmium in the marine environment. The concentration of cadmium in our study is comparable to that in the Severn Estuary where cadmium ranged between 0.11-0.4 µg/l as reported by Harper[18] (1991), Wong[24] (1980) and Ouseph[25] (1992) in Tolo Harbour and Cochin Estuary where higher concentrations (Table-1).

Lower concentration of cadmium was found in Gwadar and Bulleji seawater respectively. This concentration is 40 times lower according to USA-EPA[26] (1998) or marine water quality criteria for chronic and acute level (Table-1).

14.1.5 Chromium

The highest mean chromium concentration in seawater was found in the Karachi Harbour and Gizri creek where the concentration ranges from 2.61 and 2.13µg/l (Fig.6). High concentration of chromium is mainly due to untreated tannery waste which is being dumped in the Karachi Harbour and Gizri creek via Lyari and Malir River respectively.

14.2 Concentration and distribution of heavy metals in sediments

The results of heavy metals (Cu, Zn, Cd, Ni and Cr) in sediments that were collected from Buleji, Karachi Harbour, Korangi and Gizri and Creek Gwadar fish Harbour and off-Gwadar fish Harbour (Gwadar East Bay) are shown in Fig.7-9.
Concentration of all five heavy metals in surface sediments decrease in the following order Karachi Harbour > Korangi creek > Gizri creek > Buleji in Karachi Coastal > Gwadar East Bay >off-Gwadar East Bay.

14.2.1 *Nickel*

Nickel concentration was observed to be highest at Karachi Harbour where as its concentration was 46 ppm, and lowest at Buleji (5 ppm). About half the concentration (22 ppm) of nickel of Karachi Harbour was recorded in Gwadar East Bay sediment, the source of which may be natural of rocks (Fig.7).

This data is comparable to other parts of the world (Table-2).such as. Bombay Harbour (Patel[16],1985) Kaohsiung Harbour (Chen[27],1977) reported higher concentration of nickel in sediment compared to the Karachi coastal and Gwadar coastal areas. In contrast, lower concentrations were recorded by Soulsby[28] (1978), Salamanca[29] (1978), and Seng[14] (1978).

14.2.2. *Zinc*

The highest mean concentration of zinc in sediment was found in the surface sediments of the Karachi Harbour i.e. (192.7 ppm) while about 22 times lower concentration was found in Buleji Coast (Fig.7). In the previous studies (Monawwar[3]1995), in Karachi Harbour, concentrations were found to be almost half of recent studies. Monawwar[8],(1999) reported mean concentration levels of zinc in sediment as 35.2 ppm in Gwadar East Bay.

Comparatively the relative concentration of zinc in the Karachi Harbour was found to be higher than Bombay Harbour, Portsmouth Harbour, Conception Bay, Juru Estuary and Upper Gulf of Thailand (Table-2).

14.2.3 *Copper*

The highest concentration of copper in sediment was observed in the Karachi Harbour (89 ppm) while the lowest was recorded in Buleji (1.6 ppm) The concentration was (7.8 ppm) off Gwadar East Bay (Fig.8). Untreated waste of SITE, KITE and LITE area can be attributed to high concentration in the sediment of Karachi Harbour, Korangi and Gizri creek respectively.

Copper concentration in the sediments Karachi Harbour was found to be lower than that found in Bombay Harbour, Higher concentrations were reported in Portsmouth Harbour (Soulsby[28] 1978), Juru Estuary (Seng[14] 1987), Singapore Estuary (Sin[30] 1991), Koasiung Harbour (Chen[27] 1977), Conception Bay

Salimanica[29] (1988) Menasveta[31] (1981) in Gulf of Thailand (Table-2).

14.2.4 *Cadmium*

Highest concentration of cadmium in surface sediment was found at Karachi Harbour and Korangi creek 1.12 and 0.99 ppm respectively whereas lower values were recorded at Buleji and Gwadar East Bay 0.31 and 0.42 ppm respectively (Fig.8). Previous record (Monawwar[3] 1995) shows that concentration of cadmium in Karachi Harbour has increased up to three times in the past 8 years The concentration of cadmium in the surfacial sediments is although lower than the other geographical areas as reported by Portsmouth Harbour (Soulsby), Juru Estuary (Seng), Singapore Estuary (Sin), Conception Bay (Salamanca) and (Menasveta) in Gulf of Thailand except Koasiung Harbour (Chen). (Table-2)

14.2.5 *Chromium*

The concentration and distribution of chromium in sediments was observed to be similar pattern as Cu, Ni and Zn for this study. The mean concentration of chromium was 94.25, 27.67, 20 and 14.3 ppm recorded from the Karachi Harbour Korangi creek, Gizri Creek and Gwadar East Bay respectively (Fig.9). High concentration of Chromium can be attributed probably to large amounts of chromium being utilised (waste of tannery industries) in the Lyari River, thst ultimately enters in the Karachi coastal area via Karachi Harbour. Similar observations were noted by Papakostidis[32] 1974, who reported high chromium concentration near sewage outfall in Saronikos Gulf, Greece. The results of chromium concentration in surface sediment were comparable with the Bombay Harbour and Koasiung Harbour (Table-2).

14.3 Heavy metals in marine organisms

Heavy metals observed in the bodies of the marine organisms were mainly as a resultant of the processes of uptake and losses due to metabolic control, although the body metal concentration is also affected by changes in body weight due to growth, and reproduction, storage or depletion of energy reserves, etc. Bryan[33] (1980) Enrichment of heavy metals in the marine organisms depends on available food that is probably the major pathway of the uptake of the heavy metal and accumulation in the tissue of marine organisms. Marine organisms also have the capability to detoxify the excess of heavy metals through the formation of metal binding protein (Metallothioneins).

14.3.1 Heavy metals concentration in mussel *(Perna viridis)*

Mussels are widely distributed in the aquatic world. Mussels are rich in protein and are nutritious food. Due to its nutritious value, it becomes important commercial fisheries product of the coasts, estuaries and bays. According to Farrington[34] (1987) mussels have the capability to accumulate the excess of heavy metals from seawater up to 100,000 times higher than the seawater.

Perna viridis are generally known as green mussels and are usually, found in Arabian sea and adjacent seas. *Perna viridis* are marine bivalve with their green shells and are found in coastal waters attached to rocks and other substrate. Various species of mussels have been widely used in pollution monitoring programs such as mussels watch program. *Perna viridis* has been used as heavy metal pollution indicator species by Phillips in Hongkong, Hungspreugs[35] (1984) in Gulf of Thailand, Chidambram[36-37] (1992) in Indian coast.

Since mussels are the best accumulator of the heavy metals, therefore green mussels *Perna viridis* have been used for the assessment of the heavy metal pollution at

Karachi and Gwadar coast. The results of heavy metal concentration distribution in mussels (*Perna viridis*) have been shown in the fig.10-11.

14.3.2 *Copper*

Concentration of copper in the mussel tissues were found in the following order Karachi Harbour > Korangi Creek > Gwadar East Bay 10.32, 7.3, 6.44 (ppm dry weight) respectively (Fig.10). The copper accumulation in the mussel tissues from the current study were compared with report from different geographical areas (Table-3). It is found that the results were comparable to the mussels found in the Thailand and Oman areas however higher concentration of copper were reported from England, Wales and Scotland mussels.

16.3.3 *Cadmium*

Concentration of cadmium in mussel was found highest in following order Karachi Harbour>Korangi Creek>Gwadar East Bay 0.45, 0.34 & 0.21 ppm dry weight respectively (Fig.10). High concentration of cadmium in mussels of Karachi Harbour is due to the untreated waste from the industries and sewage that enhances the accumulation of cadmium in the mussel tissues. Similarly Phillips[38] (1992) observed high concentration of cadmium in the mussels (*Perna viridis*) in the industrially contaminated Port Phillips Bay (18 ppm dry weight).

Comparison of heavy metal contents in the mussels tissue from different regions of the world have been presented in table-3.

14.3.4 *Chromium*

Highest concentration of chromium in the mussels (*Perna viridis*) was found in

Karachi Harbour 3.77 ppm dry weight, while lowest concentration was recorded in 1.12 ppm dry weight in the Gwadar East Bay (Fig.10). Gault[39] (1983) found high concentration of chromium in the mussels of Northern Ireland near the sewage outfall and effluents of local tannery waste discharge point. High concentration in mussels are also reported by Satmadjis[40] (1983) in Sorinikos Gulf (Table-3).

14.3.5 Zinc

Zinc is one of the essential metals for the marine organisms, and it increases the enzymatic activity (Vallee[41] 1978). The concentration of zinc was found between 36-64 ppm dry weight in the study area. Highest concentration as expected was found in the Karachi harbour (Fig.11). Similar observations were recorded by Anderlin[42] (1991) near the sewage outfall at the entrance of Wellington Harbor, New Zealand.

The comparison of zinc contents in the Mussels in different coastal areas is shown in table-3. Higher contents of zinc were reported in Scotland (Devies[43] 1981), Salalah (Fowler[44] 1983), and Saronikos (Satsmadjis[41] 1983) and England & Wales (Murray[45] 1982) than the studied area except in Gulf of Thailand (Manuwadi[46] 1984) and Pitani Bay of Thailand (Evraartsts[47] 1987).

14.3.6 Nickel

Concentration of nickel in the mussel of Karachi harbour was found to be double of that found in the Korangi Creek and Gwadar East Bay (Fig.11). Fowler[44] (1983) observed similar concentration of nickel in the mussels of Omani waters, while higher concentration were reported by Satmadjis[40] (1983) in Sorinikos Gulf (Table-3).

14.4 Heavy metals concentration in fishes

The result of five heavy metals reported in fishes of Karachi harbour Korangi creek and Gwadar East Bay are shown in Fig.12-20. The species used during this study were juvenile of twelve species of fish from Karachi Harbour, eleven species of Korangi creek and fifteen species of Gwadar East Bay.

14.4.1 *Zinc*

The highest mean concentration of zinc in fishes were recorded in *Acanthopagrust*, *Gerres filamentosus*, *Terapon jerbua* of Karachi harbour, Korangi creek and Gwadar East Bay fishes respectively (Fig.13, 16 &19).

High concentration of zinc has been documented in the sediments as well as water that reflected condition of fishes of Karachi harbour and Korangi creek. Similar observations were made by Stenner and Nickless[48](1974) in the marine biota of Hardenger Fjord Norway due to high concentration background in the water and sediments. The comparison of heavy metal contents in fishes in different coastal areas is shown in Table-4 .The concentration of zinc recorded by Eustace[49] (1974), Huseyin[50] (1982) Singball[51] 1982) in the fishes of Derwent Estuary, Izmir Bay and Aguda Bay respectively were found lower than that in the Karachi Harbour.

14.4.2 *Cadmium*

Cadmium is the most toxic element after mercury for marine life as well as for human life. It is accumulated in the body of the marine organisms due to its poor regulatory ability, as recorded by Pentrath[52] (1976), Olafson[53].(1977)

The mean concentration of cadmium in the fishes was found to be 0.06, 0.04, 0.06 ppm fresh weight in the fishes of Karachi harbour, Korangi creek and Gwadar East Bay respectively. The highest concentration of cadmium was recorded both in *Sillago shiama* of Karachi harbour and Gwadar East Bay and *Carangoides oblongus* obtain from Korangi creek fish. Cadmium contents in the present study were found to be lower compared with the maximum permissible daily intake (Table-5). The concentration of cadmium in the fishes is also compared with the published results. High values were observed by Huseyin[50] (1982) Singball[51] (1982) and Kureishy[54] (1993) in Izmir Bay, Aguda Bay and Qatari coast respectively. Stenner and Nickless[55] (1992) found high concentration of cadmium in the body muscles of *Solea solea* and *Raja clavata* (2.1, 2.45 ppm fresh weight) respectively in the coastal areas of Spain and southern Portugal due to the river inflow near the industrialized inland region. Wright[56] (1976) also found high concentration of cadmium ranging between 3.4-5.4 ppm fresh weight in the fish *Patichthyes flestus* in the Severn Estuary while Hardisty[57] (1974) found cadmium that ranged between (1.1-1.7 ppm fresh weight) in the same species in the Barnstable Bay.

14.4.3 *Nickel*

The highest concentration of nickel was found in both *Sillago shiama* of Karachi harbour and Gwadar East Bay, and in *Pomadasys argyreus* of Korangi creek fish. High concentration of nickel was due to their feeding habits and both species feed on invertebrate, crustaceans and small fishes. Most of invertebrate such as crustaceans are less mobile than the fishes. They can therefore accumulate higher concentration of heavy metal from the Karachi coastal environment.

14.4.4 *Copper*

Copper is an essential metal required by the marine organisms for their enzymatic activity to meet metabolic needs. Marine organisms have the capability to regulate copper concentration according to their body requirement. Maximum concentration of copper was found in both *Sillago shiama* of Karachi harbour and Gwadar East Bay and *Carangoides oblongus* of Korangi Creek.

The concentration of copper reported in fish from different world coastal areas are given in Table-4. This comparison shows that the average concentration of copper in fish from Oman coast, Qatari coast, Derwent Estuary, Aguda Bay and Izmir Bay were higher than the values found in the present study. The average daily intake of heavy metals is given in Table-5.

14.4.5 *Chromium*

The concentration of chromium in fish found in the fish of Karachi Harbour was 0.42 ppm fresh weight, whereas maximum concentrations were recorded both in *Sillago shiama* of Karachi harbour and Gwadar East Bay. These fishes have chromium under the limit of normal daily intake as recommended in United Kingdom in the foodstuff (Mance[15] 1984)

Concentration of heavy metal contents in our coastal fishes have been compared with the maximum permissible daily intake limit (Mc-Graw Hill Encyclopedia[58] (1982), Burch[59] 1975 and GESAMP[60], 1985). These Concentrations of heavy metals are generally found within safe limit for human consumption Table-5.

14.5 Heavy metals concentration in mangrove leaves

Mangrove forest plays an important role in the productivity of the coastal estuarine environment. They serve as a breeding ground and provide shelter for the fish and shellfish of the coastal area. Rapid increase in population and industrial activities effect the ecology of mangrove ecosystem of the creek area, particularly in the vicinity of the Karachi coast. A numbers of studies have been reported with regards to the metal contamination of mangrove Leela[61] (1979), George[62] (1997), Chakarabarti[63] (1993), and Chiu[64] (1991). There is no published information available about the metal contamination of mangroves in our coastal area.

This present study provides information on the heavy metal levels in the mangrove leaves of Karachi coast. The results of the five metals in the mangrove leaves of four different sites are given in figures 21-22. There is no variation in the concentration of copper & zinc contents in the mangrove leaves of Karachi coast. Highest concentration of heavy metals was recorded in the Kemari mangrove leaves, an mean concentration of zinc and copper observed was 5.25 and 23.34 ppm dry weight respectively.

According to Elderfield[65] (1979) heavy metals precipitated with iron forms polysulfide mineral particularly with copper and zinc. Similar formation can be observed in the Karachi Sandspit backwater mangrove which receives considerable amount of untreated domestic wastes containing high concentration of heavy metals. Concentration of copper and zinc concentration in Karachi mangrove leaves was found to be lower than reported by Chakarabarti in Sundarbun, George in Kerala India, Leela in Ganapatipule India (Table-6).

Highest concentration of cadmium was recorded in the Karachi Harbour (Sandspit back water) 0.305 ppm dry weight and Korangi Creek area (Rehri Goth) concentration was 0.249 ppm dry weight. Concentration of cadmium was three times lower than the Sunderbun mangrove leaves. Low concentration in mangrove leaves suggested that cadmium is mostly unavailable for the uptake by plants and that uptake is inhibited by the presence of large amount of other metal ions especially zinc presence in the sediment (Thornton[66], 1981).

Concentration of Chromium and nickel was found highest in Sandspit backwater of Karachi Harbour and its concentration was recorded 6.15, 2.91and 3.04, 3.83 ppm dry weight respectively**.** High concentration of chromium reflected water and sediment concentration in Karachi Harbour.

14.6. Heavy metals concentration in seaweeds

Seaweeds and algae are best indicators of metal in the coastal waters due to their ability to reflect the concentration of metals present in the environment, (Sanchiz[67] ,1999, Eide[68] 1983, Phillips[69] 1977 and Munda[70] 1991). Only one study on heavy metals in Sindh coast has been reported in seaweeds by Jaleel[71] (1983) .

In the present investigation five metals were determined in the eleven species at two different sites of Manora (Open sea side) and Buleji. The results of heavy metal contents in the seaweeds are shown in fig.23-27.

Highest concentration of copper was found in the *Calpomonia sp*. At both the sites of Manora and Buleji, concentrations were 8.66 and 7.11 ppm dry weight respectively. Higher concentration was also observed by Munda and Shiber[72] (1980) in the same species in the Adriadic sea (22 ppm dry weight) and Ras Beirut, Lebanon (11-41 ppm dry weight).

The small variation was observed for Chromium in all seaweeds (except *Calpamonia sp*. and *Botrocladia laptopodia*) with the minimum and maximum values ranging from 2 to 3 times. Comparable concentration was observed by Shiber in the Ras Beirut Lebanon (2-11 ppm dry weight).

Highest mean concentration of cadmium was found in *Coelarthrum muelleri, Padina povina* and *Calpamonia sp*. from the seaweeds samples collected from of Manora and its concentrations were 3.41, 3.11 and 3.06 ppm dry weight respectively.

Zinc is essential element for the cell metabolism of seaweeds. In the present study highest concentration were observed in the *Calpamonia sp*. and *Ulva lactuca* (41, 38 ppm dry weight) respectively. Concentration of zinc was almost three times higher in Manora seaweed than in the seaweeds of Buleji (38 and 14 ppm dry weight). The results indicate that *Ulva lactuca* has a higher capacity for zinc accumulation from the surrounding environment. Similar observation was observed by Y.B.Ho[73] (1990) in the Hong Kong rural and urban sites where the concentration was 27 and 66 ppm dry weight respectively.

Chromium was found in similar distribution pattern in both *Calpamonia sp.* and *Botrocladia laptopodia* observed and their concentration were 13.3, 9.92 ppm dry weight (fig.27). Shiber reported higher values in *Calpamonia sp.* of Ras Beirut Labanon (28.7 ppm dry weight)

Comparing the results of metal accumulation with those from the other areas as discussed above, the seaweeds of Manora were found to have accumulated metal, partially due to untreated industrial and domestic waste entering in marine coastal environment through the Lyari River from the city.

15.Conclusion & Recommendations:

Conclusions

- Highest Concentration of metals in water and sediments was observed in Karachi Harbour area followed by; Korangi creeks> Gizri creeks> Gwadar fish Harbour> Off Gwadar East Bay>Buleji.

- Heavy metals accumulation was observed to be twice in concentration two times more of Heavy metals in green mussels of Karachi Harbour as compared to that of Gwadar East Bay.

- Within Karachi Harbour, highest accumulation was observed for Zn, Cd, and Cu in shellfish (*Sepia sp*.) and Ni & Cr in fish (*Sillago sihama)*.

- In Gwadar East Bay highest accumulation was recorded in *Sillago sihama* for Ni, Cu, Zn, Cd and Cr, while in Korangi creek *Carangoides oblongus* higher accumulation was observed for Cd and Cu.

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- At present the heavy metal concentrations studding undertaken in the respective fishes etc. were within the safe limits.

- For Mangrove higher accumulation of Cd, Cr and Ni was observed in mangrove leaves of Sandpit back water (Karachi Harbour), while highest concentration of Cu & Zn was recorded in Kemari backwater and Rehri Goth (Korangi Creek).

- Amongst seaweeds higher accumulation of Cd was found in Red seaweed (*Botrocladia laptopodia).* Highest accumulation of Zn, Cu, and Ni & Cr was recorded in Brown seaweed (*Colpamonia Sp*.) Cu & Zn were found in Green seaweed (*Ulva faciata)*.

- Generally the concentration of heavy metals found in fish and shellfish are found to be lower when compared with the results published for tropical region.

Recommendations

1. Continued monitoring of heavy metals of Karachi Harbour and Korangi creek should be undertaken commercial important fish and shellfish.

2. National environmental quality standards for water quality and toxic metal content in fish and shellfish should be formulated and implementation.

3. A programme should be prepared for the monitoring of organic and inorganic pollutant along the coast of Pakistan.

4. Upgrade the existing sewage treatment capacity of treatment plant at Karachi and other coastal areas to treat the sewage and industrial wastes water.

16.Output: List of reports, media articles slides, photographs etc.

The results will be published in scientific journal and author of this report will write popular science article.

17. Equipments status report:

The instruments that were used in the present study were the property of the National Institute of Oceanography. However, the funds provided by WWF-Project were utilized for collection of samples and the purchase of the consumable for Atomic Absorption spectrometer.

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