XA9848335

THE APPLICATION OF STABLE CARBON ISOTOPE RATIOS AS WATER QUALITY INDICATORS IN COASTAL AREAS OF KARACHI, PAKISTAN

R.M. QURESHI, A. MASHIATULLAH, T. JAVED,
M.A. TASNEEM, M.I. SAJJAD
Environment Research Group, PINSTECH, Islamabad

M. SALEEM, S.H. KHAN, S.H.N. RIZVI
National Institute of Oceanography, Karachi

S.A. SIDDIQUI, R. QARI
Centre of Excellence in Marine Biology,
University of Karachi, Karachi

Pakistan

Abstract *- Stable carbon isotope ratios ($\delta^{13}C$) of total dissolved inorganic carbon (TDIC), total inorganic and organic carbon in bottom sediments, as well as sea plants in polluted water sources, non-polluted Karachi Sea water and pollution recipients are used to elaborate pollution scenario of shallow marine environment off Karachi coast. These results are supplemented with stable isotope composition of nitrogen ($\delta^{15}N$) in seaweeds and mangroves, toxic/trace metal concentration in sea-bottom sediments, total Coliform bacterial population, electrical conductivity, temperature and turbidity. Isotopic data shows that the mangrove ecosystem and the tidal fluctuations play a key role in controlling contamination inventories in shallow sea water off Karachi coast, specifically the Manora Channel. The Karachi harbour zone is found to be the most heavily polluted marine site in Manora channel during high as well as low tide regimes. Significant concentrations of toxic metals such as Pb, Ni, Cr, Zn, V, U are observed in off-shore sediments of Karachi coast. The results show that sewage and industrial wastes are the main sources of heavy metal pollution in Karachi Harbour, Manora Channel exit zone and the southeast coast. However, as compared to other coastal areas, the Karachi coast is moderately polluted. Studies suggest incorporation of quick remedial measures to combat pollution in shallow marine environments off Karachi Coast.*

1. SIGNIFICANCE OF OVERALL PROBLEM

Seawater of the coastal regions near large industrial and population centers normally receives large quantities of sewage and industrial waste water which pollutes the living and recreational environments of coastal waters. Karachi is located on the northern boundary of the Arabian Sea. It is the largest city in Pakistan with coast line extending up to about 30 km. It is estimated that nearly 300 million gallons per day of domestic and industrial waste water is generated. This waste water is drained into Karachi sea mainly via Layari River, Malir River/Ghizri Creek and Korangi Creek (Fig. 1).

Manora Channel is a navigational channel and it connects the Karachi Port with the Arabian Sea in the south (Fig. 2). It spreads over an area of 7.17 km and includes the Karachi Harbour and the Keamari Fish Harbour. About 3.4 million cubic meter water enters and leaves the channel during a tidal cycle. The channel entrance is narrow and easily silted. The

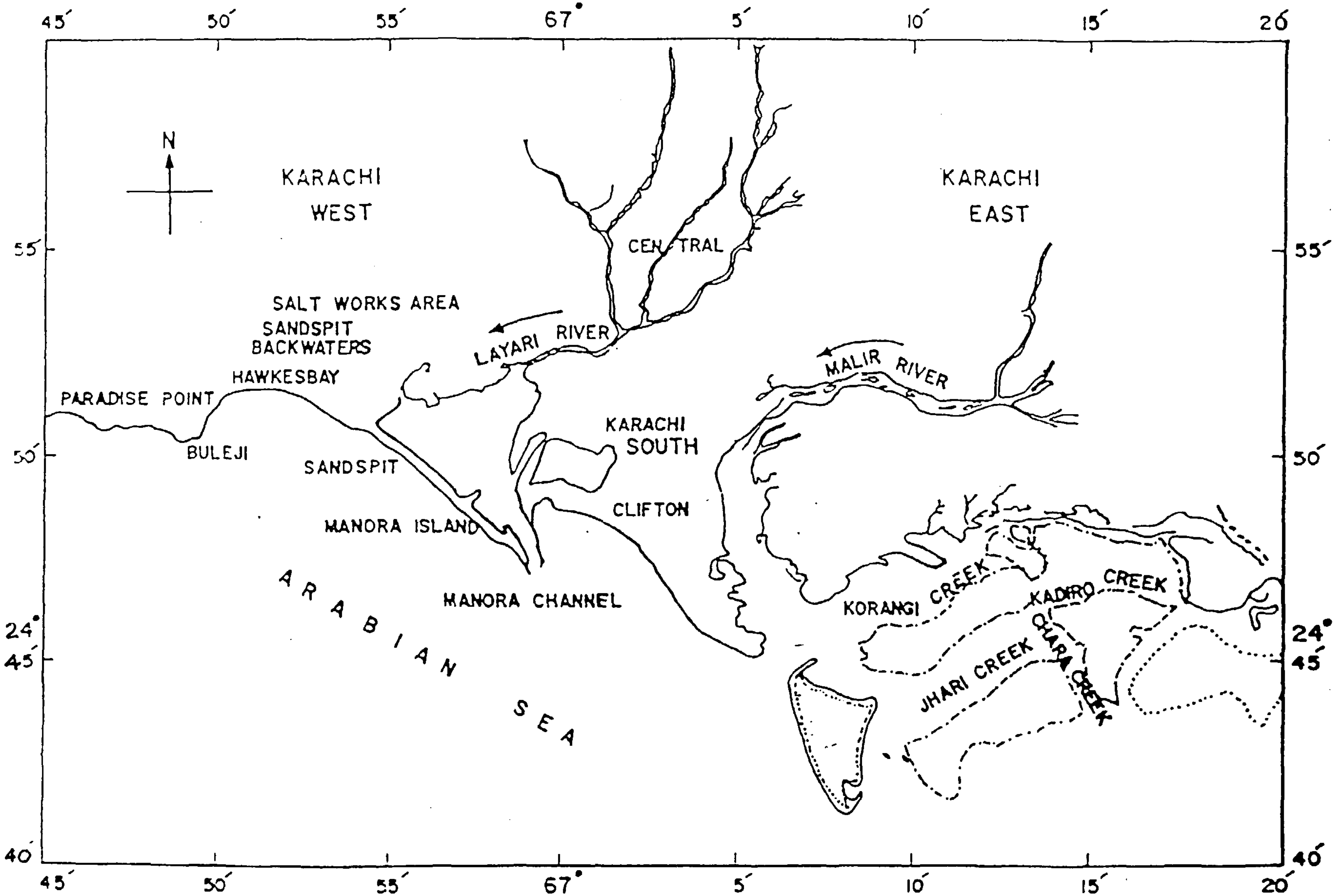

Fig. 1 Coastal map of Karachi (Pakistan) indicating polluted rivers drainage course in Manora Channel and Ghizri/Korangi Creek.

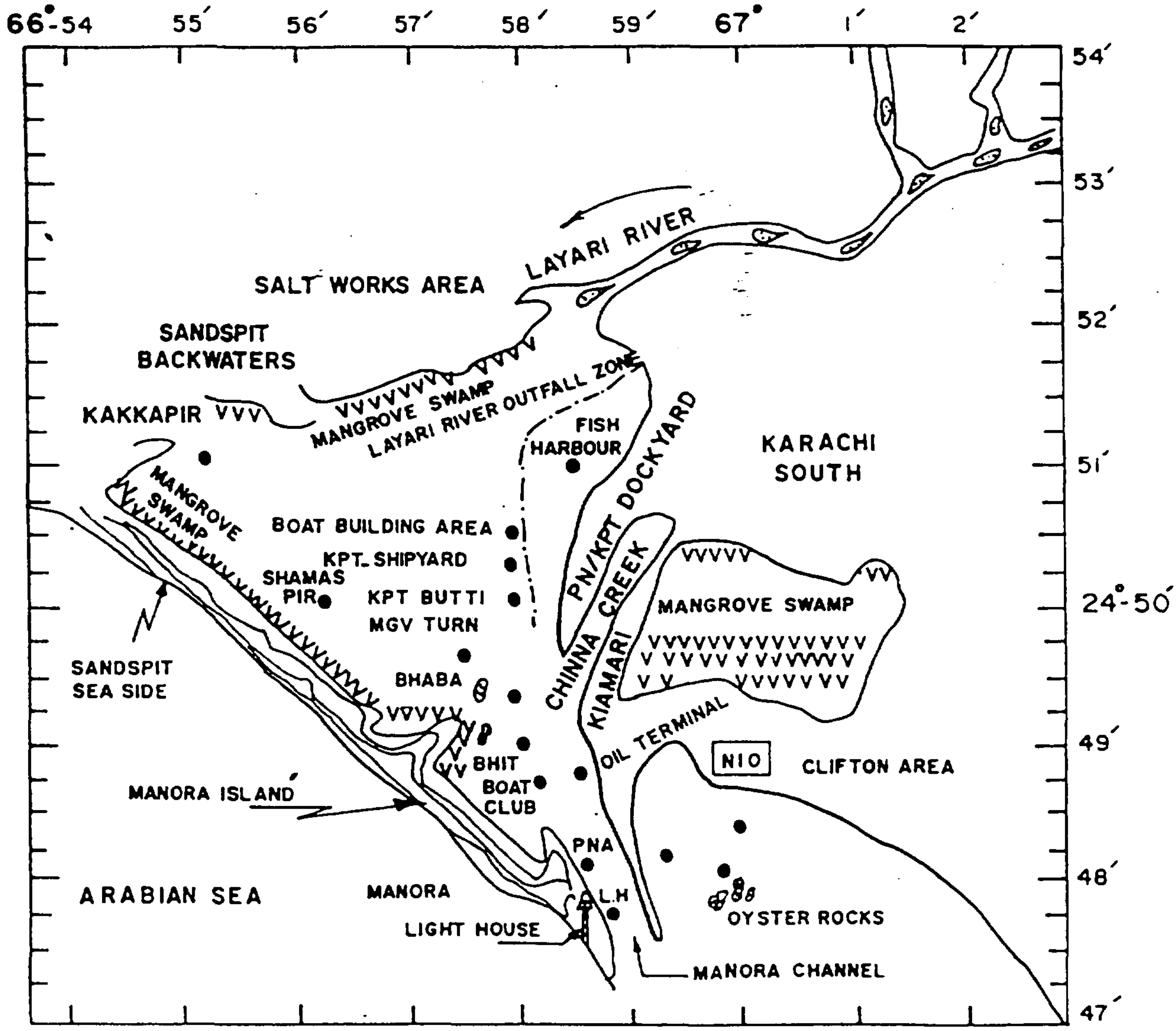

Fig. 2 Details of sampling points in Manora Channel & Karachi harbour.

addition of sediments in the Karachi harbour area is mainly brought by the Layari River and the status of sediment input load is so bad that the channel has to be dredged year round. About 45600 cubic meters of silt is removed from the channel annually, therefore, its depth is maintained by regular dredging throughout the year. River Layari flows through urban centers, where it is loaded with sewage/effluents of domestic origin from the north-western areas of Karachi and of industrial origin from the Sind Industrial Trading Estate (S.I.T.E.). Ultimately, the Layari River discharges large quantities of untreated and semi-treated domestic wastes on the north-western end of the Manora Channel. The Layari River outfall waters thus contain significant inorganic pollution in terms of sulfates, nitrates, carbonates, calcium, allum, magnesium, arsenic, and heavy metals and organic pollution mainly pesticides, herbicides, PCB's, cyanides, PAHC's, and plasticizers, cresols, floating plastics particles etc. The suspended matter is said to reach the coast at an average rate of 30 tones/day. Karachi Harbour/Manora Channel receives a variety of chemicals such as calcium carbonate (115.74 metric tonnes/day), total dissolved solids (317 metric tonnes per day) and iron oxides (5.14 metric tonnes per day). The quantity of domestic wastes produced per household in Karachi varies from 100 to 280 liters per day. The abiological and biological dissolution of organic matter in bottom sediments of Manora channel also add to the deterioration of water in the channel. It is an overcrowded port and an estimated 3900 ships leave and enter the port annually. About 19.1 million tonnes cargo is handled including the oil. The Manora Channel also has a Naval Port and a Fish Harbour. Cargo ships, fish trawlers and mechanized boats of national and international origin pump-out dirty bilge and sludge into sea water. Cleaning of oil tankers at harbour is responsible for the discharge of the washings along with all contaminants which ultimately enter the sea. Fish market and fish processing plants at the fish harbour also discharge their solid wastes and effluents directly into the Manora channel. Upchannel environment also receives untreated domestic wastes from five villages located at Manora Island, Bhaba Island, Bhit Island, Shams Pir and Kakka Pir.

Manora Channel area is now considered to be the most heavily polluted marine site in Pakistan. Some sporadic and small scale pollution surveys involving classical hydro-geochemical and/or biological techniques have been made in the past to estimate the pollution status along the coast of Karachi [1, 2, 3, 4]. The fish habitat and the mangroves in the Manora Channel/Karachi harbour and backwater areas are now under considerable stress. It has been documented that the discharge of sewage and industrial pollutants in the Karachi harbour/Manora Channel has not only caused depletion of the Oyster beds in and around Karachi harbour area but the shrimps and fishes which were abundant in the Manora Channel, Manora Seaside and Hoxbay area have migrated to the deeper waters [5, 6]. Nevertheless, inspite of very high pollution levels in the Karachi Harbour area, it is still being used for bathing by tourists and the local population. The southeast coast of Karachi is mainly polluted by drainage of Malir River/Ghizri Creek and Korangi Creek domestic sewage and industrial waste effluents.

2. PRESENT INVESTIGATIONS

2.1 Objectives

The main objective of this paper is to document for the first time conjunctive use of environmental stable carbon isotope techniques and classical non-nuclear analytical techniques for evaluation of the shallow marine pollution trends off Karachi coast with special reference to the Manora Channel / Karachi Harbour area. Studies include determination of stable carbon isotope ratios ($\delta^{13}C$) of (i) total dissolved inorganic carbon (TDIC), (ii) total inorganic and organic carbon in bottom sediments, (iii) sea plants (mangroves & seaweeds); stable isotope composition of total Kjeldahl nitrogen ($\delta^{15}N$) in seaweeds and mangroves, toxic/trace metal concentration in sea-bottom sediments, total Coliform bacterial population, electrical conductivity, and turbidity in polluted water sources (Layari River downstream and outfall zone), non-polluted Karachi Sea water and pollution recipients (Manora Channel, Karachi Harbour and its backwaters).

2.2 Sampling and Analysis

Field sampling was performed at various interval of time during the period from April 1995 to September, 1997. This period was selected to cover the possible spectrum of changes in pollution transport pattern due to seasonal variable winds of the monsoon system. During the winter (October- February), the northwest monsoon winds are relatively weaker, resulting in diminishing upwellings along the western margins of the Arabian Sea [6]. During the northwest monsoons (October-February), the seawater from the nearshore and offshore Indus Delta enters the coastal waters of Karachi from the southeast and moves along the coast towards the northwest or westwards and then to the western coast of Karachi [7]. The first sampling was performed in May 1995, the second sampling from 11-18 January 1996, the third sampling from 4-6 December 1996 and the fourth sampling from 24-27 September 1996.

Mangroves, seaweeds, sediments, and high tide and low tide water samples were collected from *polluted water sources* and *pollution receiving bodies* namely: (i) Manora Channel, (ii) South-East Coast of Karachi (Clifton-Ibrahim Haideri Coastline), (iii) Oyster-Rock Zone /Manora Channel Exit (iv) North-West Coast of Karachi (Manora seaside-Paradise Point Coastline), and (v) non-polluted region of Karachi-sea. In order to elaborate on pollution levels of Karachi harbour area, water samples were collected during the last hour of low tide regime along 5 profiles perpendicular to the KPT-Shipyard and Naval Dockyard starting from the open highlands facing Layari mangrove forests to the Bhaba Island. In the Manora Channel mains, water samples were also collected at three intervals between peak high tide to peak low tide period. The polluted rivers were approached by road during the low tide period whereas sampling in the Manora Channel/Karachi Harbour was performed using conventional mechanized tourist Boat. Sediment samples were collected with the help of a conventional Peterson Grab and contained in high quality polyethylene bags. Pre-treated mangrove leaf and seaweed samples were obtained from Centre of Excellence in Marine Biology (CEMB), University of Karachi, Karachi. Water samples have been collected within 10 m depth contour.

The location of sampling points was determined with the help of a Garmin GPS-100 Personal Navigator™ (M/S Garmin, 11206 Thompson Avenue, Lenexa, KS 66219). In-situ measurements of turbidity, electrical conductivity (E.C.), temperature were performed on all water samples. The time for the occurrence of a low or high tide was deduced from the standard TIDE TABLE GUIDE-1995 as published by the Pakistan Navy. Turbidity was measured with a battery operated portable turbidimeter (Model 6035, JENWAY). Electrical conductivity and temperature were measured with a portable conductivity meter (Model HI 8633, M/S HANNA Instruments). Water samples for stable carbon isotope analysis were collected in leak-tight doubled stoppered plastic bottles and spiked with 0.1M $HgCl_2$ solution to eliminate bacterial activity for preservation of TDIC.

All samples were stored in the laboratory under cooled conditions prior to analysis. Total Coliform bacteria (E.Coli/100 ml water sample) were determined within 24 hours of sample collection using a dual incubator (PAQUALAB Model 50, ELE International, U.K.). Water samples for stable carbon isotope analysis were filtered firstly through Whatman-42 filter papers and then through 0.45 micron nitrocellulose filters. Sample preparation for stable carbon, and nitrogen isotope analysis of TDIC, inorganic fraction in the sediments, and organic fraction in seaweed & mangrove samples was performed according to standard procedures [8, 9]. Stable isotope analyses were performed using Mass Spectrometers and expressed as delta (δ) per mil (‰) values relative to international standards namely: PDB (Pee-Dee Belemnite) for ^{13}C analysis, Air-N_2 for ^{15}N analysis (reproducibility better than 0.1 ‰ PDB for $\delta\,^{13}C$ and 0.2 ‰ Air-N_2 for $\delta^{15}N$ measurements). Selective toxic/trace element analyses (except uranium analysis) of dried/pulverized sediments (80 mesh size) are performed with ICP-OES (Model 3580, Applied Research Laboratories, Switzerland) using standards namely SL-1, SL-3 and Soil-5 as well as with Flame Atomic Absorption Spectrophotometer (Perkin Elmer Model 3300, only for Cu, Cr, Ni, Pb, Zn) and Graphite

Furnace Atomic Absorption Spectrophotometer (Model HGA-600, only for Cd analysis). The concentration of uranium in sediments was measured with a 26-000 Jerrel Ash Fluorometer.

3. RESULTS AND DISCUSSION

3.1 Water pollution profiles

3.1.1 Input functions of pollution sources: Electrical conductivities of polluted river outfall zones are much less than the non-polluted Karachi sea waters. Converse is true for Coliform bacterial population and turbidity. E.Coli, E.C., turbidity and temperature of the Layari River downstream water prior to outfall in Karachi harbour/Manora Channel are respectively in the range of: >300 coliform counts per 100 ml, 2.1-2.96 mS/cm, 6.15-37.6 NTU and 20.5 - 28.7 °C. Similarly, for the Layari River outfall area towards Karachi Harbour, E.Coli, E.C., turbidity and temperature were: >300 coliform counts, 21.5 - 52.7 mS/cm, 4.2 - 68.3 NTU and 20.2 - 27.8 °C respectively. E.Coli, E.C., turbidity and temperature of the Malir River downstream water prior to outfall in Gizri/Korangi Creek are respectively in the range of: >300 coliform counts per 100 ml, 3.8 - 6.2 mS/cm, 7.8 - 26.6 NTU and 19.9 - 27.8 °C. Similarly, for the Malir River outfall area viz. Gizri/Korangi Creeks, E.Coli, E.C., turbidity and temperature were: >300 coliform counts, 3.2 - 44.9 mS/cm, 8.4 - 38.6 NTU and 20.8 - 27.6 °C respectively. For the Karachi Sea, E.Coli, E.C., turbidity and temperature were: ~175 Ecoli/100 ml , 52.9 - 55.6 mS/cm, 1.06 - 6.7 NTU, 20.1 - 21.2 °C respectively. pH was measured only during the first sampling phase whereas, coliform population was measured for the first two sampling phases. Layari River has pH value lower than the Malir River/Gizri Creek. The Layari River outfall has pH values in the range of: 8.14 - 8.36. Carbon isotope composition of the TDIC in polluted river water is also quite distinctive. The Layari River has a $\delta^{13}C$ values in the range of -6.9 to -2.6 ‰ PDB. The Malir River has a $\delta^{13}C$ values in the range of - 9.6 to -4.2 ‰ PDB. Malir River outfall zone (Ghizri/Korangi Area) has $\delta^{13}C$ values in the range of -8.9 to -2.3 ‰ PDB. The Karachi sea blue waters have a $\delta^{13}C$ value in the range of -0.79 to +0.6 ‰ PDB (Table-I). However, it is interesting to note that although, electrical conductivity of polluted Layari River outfall increases significantly due to large scale mixing of sea water, the Layari river outfall zone has quite depleted $\delta^{13}C$ values (ranging from: -4.3 to -10.2 ‰ PDB) as compared to the polluted Layari river waters and the Karachi sea blue waters. In fact, its average $\delta^{13}C_{TDIC}$ composition is comparable with that for Layari River downstream. This is attributed to the impact of mangrove swamps in the Layari River outfall zone. As soon as, the high tide gushing waters enter the mangrove swampy areas, they dissolve isotopically depleted CO_2 which is biogenically produced in mangrove swamps during high/low tide regimes (duration: ~ 6 hours each). This may be clarified by the neap tide $\delta^{13}C$ values in the Layari River outfall zone, which are relatively enriched in ^{13}C as compared to the spring tide regime values. These average $\delta^{13}C_{TDIC}$ values of the Layari River outfall zone are, therefore, taken as inorganic carbon isotope input functions of Layari River outfall for evaluation of mixing characteristics of polluted Layari River mouth waters in Manora Channel.

3.1.2 Carbon isotopic evaluation of pollution: The conventional physio-chemical and biological measurements not only lack in high precision but these also do not reflect on the type of pollution source. On the other hand, stable carbon isotope analysis of TDIC have not only high precision of measurement (better than 0.1 ‰ PDB) but the inputs due to various pollution sources and the types can be realized by their characteristic $\delta^{13}C$ range. These data are discussed in the following section.

3.1.2.1 Manora channel pollution profile: The Manora Channel consists of stations from Keamari Fish harbour in West Wharf Area to Manora Lighthouse exit near Naval Radar post. The pollution profile of this area is discussed in the following section in terms of two sub-profiles.

Karachi Harbour Sub-Profile: The Karachi Harbour sub-profile (zone between Layari River Mouth & Naval Dockyard/Bhaba-Bhit Island) is the main recipient of pollution load brought by Layari River, its tributaries and the mangrove swamps. Total coliform counts are more than 300 per 100 ml in almost all the samples taken from the main harbour area during the lowest and the highest tidal conditions. These high levels of coliform render the harbour waters unfit for bathing activities. No uniform distribution of E.Coli was observed during the lowest tide conditions in the harbour area. Electrical conductivity is in the range of 44 - 50 mS/cm during the highest tidal conditions and 32 - 52 mS/cm during lowest tidal conditions. A decrease in E.C. at lowest tidal conditions is attributed to large scale mixing of Layari River outfall water with the Karachi sea water in the harbour area. Turbidity levels during calm sea regimes (January-December) are normally lower than the values for the rough sea period (August-September). In general, turbidity levels during high tide regimes are lower than the values measured for low tide periods due to dilution caused by inputs of relatively less turbid sea water. No specific differences in temperature were observed during the lowest to highest tidal conditions. It is apparent that the relatively more enriched $^{13}C_{TDIC}$ values in the Karachi Harbour channel at high tide conditions are replaced by quite depleted $\delta^{13}C_{TDIC}$ values at low tide condition, thereby, indicating a fair proportion of the pollution inventory from Layari River outfall area into the Karachi Harbour/Manora Channel during low tide regime. The physiochemical and bacteriological analysis have given a rough evaluation of the aerial extent of the polluted zone in the Karachi harbour area in response to mixing of Layari River water with the Karachi Sea water under high and low tide conditions. Further studies were carried out to identify the boundary of high and low pollution zones in the Karachi Harbour area during last hour of the low tidal regime (Table-II). For this purpose five pollution profiles were tracked across the Karachi harbour channel starting from the Karachi Port Trust building down to the Bhaba Island. Table-III presents the findings of this exercise. It is evident that the more polluted zone is characterized by fairly negative $\delta^{13}C_{TDIC}$ values. Slight increase in the $\delta^{13}C_{TDIC}$ values at the extreme of Layari Outfall Channel close to the KPT Shipyard boundary are attributed to the overspill and addition of relatively clean sea waters retreating from the Keamari Fish Harbour Channel at low tide condition. This influx of sea water in the Layari River Channel of Karachi Harbour zone may also be verified by a corresponding increase in the E.C. values for these samples.

Manora Channel Mains sub-profile:The Manora Channel Mains sub-profile (zone between Boat Club & Manora Lighthouse), electrical conductivity values range between 44.1 - 46.9 mS/cm during low tide conditions and 50.1 - 52.8 mS/cm during high tide conditions. Turbidity levels range between 7.9 - 19.4 NTU during low tide conditions and 2.1 - 14.3 NTU during high tide conditions. Similarly, coliform bacterial population ranges between 179 to 258 & >300 for high and low tide regimes respectively. No uniform distribution of E.Coli was observed during the lowest tide conditions in the harbour area and the Manora Channel Mains. Occasionally, the physiochemical and carbon isotope data of samples collected in the vicinity of Bhaba/Bhit Islands and Pakistan Naval Academy (PNA) are off-set due to influx of sewage from these residential zones. In order to further elaborate on the findings, samples were collected at three intervals during the low tide regime at various locations along the Manora Channel Mains. The first sample was collected as the high tide

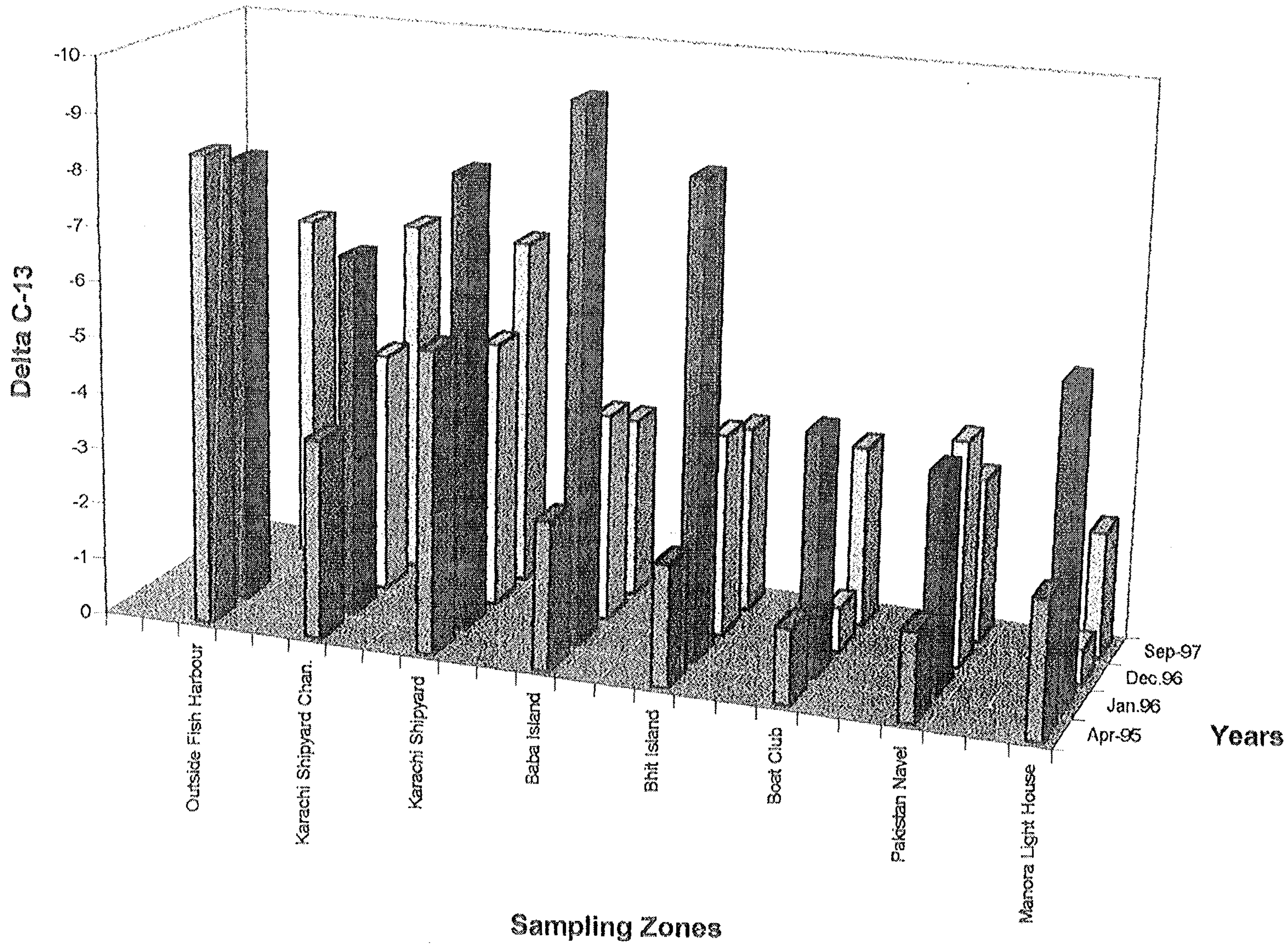

Fig. 3: Evolution of $^{13}C_{TDIC}$ in Karachi Harbour/ Manora Channel (1995-1997)

started lowering. The second sample was taken at the middle of low tide regime. The third sample was taken at the lowest of tide level. Results are presented in Table-IV. It is evident that pollution inventories at each measuring stations increase with the decrease in tide level. Further the severity of pollution decreases as we move out of the channel towards open sea.

Fig. 3 shows a overall scenario of evolution of $\delta^{13}C_{TDIC}$ values for the Karachi Harbour/Manora Channel for the four sampling phases under low tidal conditions.

***3.1.2.2 Oyster Rocks-Manora Channel Exit Profile*:** Oyster Rocks are located in open sea close to entrance of Manora Channel facing Clifton beach. The *Oyster Rocks profile* includes stations namely: KPT Oil Jetty, Oyster Rocks and the shore-line facing National Institute of Oceanography (NIO) & Marina-Heights. Here electrical conductivity values range between 48.0 - 49.2 mS/cm during low tide conditions and 59.7 - 51.7 mS/cm during high tide conditions. Turbidity levels range between 4.8 - 7.9 NTU during low tide conditions and 2.0 - 3.9 NTU during high tide conditions. Total Coliform counts range between 0-35 counts per 100 ml and $\delta^{13}C_{TDIC}$ values range between -1.8 to -2.7 ‰ PDB during low tidal conditions. Although, this area is much flushed by open sea waters, slightly high proportions of pollution between NIO-Oyster Rocks & Marina-Heights are attributed to impact of waste discharge from local sewage drains near KPT Oil Terminal close to the end of Clifton Beach.

***3.1.2.3 South-East Coast Pollution Profile*:** The South-East Coast of Karachi faces open sea and extends from Clifton beach near KPT Oil Terminal to Ibrahim Haideri Fish Harbour in Korangi Industrial area. Here, electrical conductivity values range between 42.9 - 46.5 mS/cm during low tide conditions (only up to Gizri Creek area) and 47.1 - 51.7 mS/cm during high tide conditions. Turbidity levels range between 3.6 - 11.7 NTU (only up to Gizri Creek area) during low tide conditions and 1.7 - 7.52 NTU during high tide conditions. Significantly high values of Coliform counts: ~100 to >300 are observed all along the coast. The $\delta^{13}C_{TDIC}$ data may be discussed in two sub-profiles. The *Clifton sub-profile* includes stations from Marina Plaza (White Pyramid Building) to start of Gizri Creek area. This area is quite flushed by sea tides.). Slightly high pollution levels near Naval Jetty are attributed to impact of waste discharge from local sewerage drains. During extreme low tide conditions, the $\delta^{13}C_{TDIC}$ of Clifton Casino is -4.39 ‰ and in Gizri Creek zone -8.1 ‰ PDB indicating significant pollution level. The *Korangi sub-profile* includes stations from start of Korangi area to Ibrahim Haideri Fish Harbour. Here, $\delta^{13}C_{TDIC}$ values are in the range of -1.05 to -6.79 ‰ PDB. Due to occurrence of a storm, it was not possible to collect low tide water samples in this area. However, samples collected at the shore-line during low tide regime indicate increasing pollution levels for various locations along this sub-profile. Tables-V present results of time evolution of pollution mixing trends at these locations. It appears that pollution levels increase during a shift from highest to lowest tide regime, thereby indicating influx of pollution from on-shore pollution sources.

***3.1.2.4 North-West Coast Pollution Profile*:** The North-West Coast of Karachi faces open sea and extends from Manora Light-House (sea side) to Paradise/Sunehry Point area. Here electrical conductivity values range between 48.2 - 52.9 mS/cm during low tide conditions and 48.6 - 52.9 mS/cm during high tide conditions. Turbidity levels range between 1.5 - 2.7 NTU during low tide conditions and 0.9 - 1.5 NTU during high tide conditions. Significantly high Coliform counts are also observed. Here, $\delta^{13}C_{TDIC}$ values are in the range of +2.4 to -

Table-I Physiochemical and stable carbon isotope input functions of polluted rivers and pollution recipients along the coast of Karachi- Pakistan (1995-1997)

Sampling Zone		Temp. (Deg. C)	E.C. mS/cm	pH	Turbidity NTU	Total Coliform	$\delta^{13}C$ (‰ PDB)
Layari River Downstream (pre outfall in harbour)	Range	20.5-28.7	2.1-2.96	7.07	6.15-37.6	>300	-6.89 to -2.55
	Average (n=4)	24.2	2.56	7.07	20.5	>300	-5.22
Malir River (pre outfall)	Range	19.9-27.8	3.8-6.2	7.7	7.8-26.6	>300	-9.5 to -4.20
	Average (n=4)	24.05	4.84	7.7	16.58	>300	-7.40
Layari River Outfall (Karachi Harbour)	Range	20.2-27.8	21.5-52.7	8.14-.36	4.2-68.3	>300	-10.22 to -4.3
	Average (n=13)	47.87	40.65	8.25	27.39	>300	-7.39
Ghizri Creek	Range	20.8-27.6	3.2-44.9	-	8.4-38.6	>300	-8.9 to -2.31
	Average (n=3)	24.275	23.36	-	22.83	>300	-5.72
arachi Sea	Range	20.1-21.2	52.9-55.6	-	1.06-6.7	~ 175	-0.79 to -0.60
	Average (n=4)	20.65	54.27	-	3.19	-	0.0625

* N.D. = Not measured

Table-II Physiochemical, bacteriological and stable carbon isotope analysis of water samples taken across apparent pollution mixing boundary in Karachi Harbour/ Manora Channel at lowest tide condition. (Date: 2-5-1995)

Profile Description	Latitude/ Longitude	E.C. (mS/cm)	Turbidity (NTU)	Total Coliform	$\delta^{13}C$ ‰ PDB
Bhaba Island					
Outside mixing boundary	N 24-49-35 E 66-57-55	52.4	5.6	NIL	-5.23
Inside mixing boundary within Layari channel	N 24-49-34 E 66-57-52	50.3	7.4	>300	-8.03
Naval Dockyard					
Outside mixing boundary	N 24-49-51 E 66-57-50	51.4	5.6	12	-10.49
Inside mixing boundary within Layari channel	N 24-49-53 E 66-57-51	49.6	10.5	>300	-9.45
Karachi Shipyard					
Outside mixing boundary	N 24-50-06 E 66-57-54	51.6	4.98	50	-18.14
Inside mixing boundary within Layari channel	N 24-50-07 E 66-57-54	50.8	9.8	>300	-11.08

Table-III $\delta^{13}C$ pollution profile tracking across Karachi harbour channel (April 1995)

Profile Description	Sampling time	Latitude	Longitude	E.C. (mS/cm)	Turbidity (NTU)	Total Coliform	$\delta^{13}C$ (‰ PDB)
PROFILE-1(A): Location: In between Boat building Area and Karachi Shipyard. Date: 30-4-1995							
Prior to apparent mixing boundary	1530 hrs.	N 24-50-23	E 66-57-47	45.4	5.41	>300	-4.01
Prior to apparent mixing boundary	1540 hrs.	N 24-50-20	E 66-57-52	53.4	5.25	36	-4.2
Just before mixing boundary	1550 hrs.	N 24-50-19	E 66-58-00	49.5	16.2	>300	-6.72
At apparent mixing boundary	1600 hrs.	N 24-50-18	E 66-58-04	43.4	29.8	>300	-9.58
Middle of Layari outfall channel	1610 hrs.	N 24-50-15	E 66-58-05	46.5	11.8	>300	-9.47
Extreme of Layari outfall channel	1620 hrs.	N 24-50-21	E 66-58-03	50.4	8.2	>300	-6.73
PROFILE-1: Location: Opposite Karachi Shipyard , Date: 26-4-1995							
Prior to apparent mixing boundary	1400 hrs.	----------	----------	53.0	7.9	176	-4.42
Prior to apparent mixing boundary	1410 hrs.	----------	----------	52.8	5.08	216	-5.64
At apparent mixing boundary	1415 hrs.	----------	----------	53.8	6.02	> 300	-9.72
Middle of Layari outfall channel	1420 hrs.	----------	----------	39.4	25.5	> 300	-10.22
Extreme of Layari outfall channel	1425 hrs.	----------	----------	45.6	27.7	> 300	-8.6
PROFILE-2 Location: Karachi Shipyard close to Butti, Date: 30-4-1995							
Prior to apparent mixing boundary	1630 hrs.	N 24-50-08	E 66-57-42	49.6	8.2	20	-4.42
Prior to apparent boundary	1635 hrs.	N 24-50-03	E 66-57-51	51.7	8.4	24	-4.9
Just before mixing boundary	1642 hrs.	N 24-50-01	E 66-57-57	47.4	18.5	NIL	-9.71
At apparent mixing boundary	1652 hrs.	N 24-49-59	E 66-58-01	49.5	23.5	20	-10.62
Middle of Layari outfall channel	1711 hrs.	N 24-50-01	E 66-58-04	51.6	9.5	>300	-9.59
Extreme of Layari outfall channel	1700 hrs.	N 24-50-00	E 66-58-04	50.4	13.6	>300	-9.61
PROFILE-3 Location: In between Bhaba Island Mangroves and Shipyard/Navel Dockyard Boundary, Date: 30-4-1995							
Prior to apparent mixing	1515 hrs.	N 24-49-49	E 66-57-29	46.1	9.4	36	-3.68
Prior to apparent boundary	1525 hrs.	N 24-49-52	E 66-57-36	46.5	8.7	NIL	-5.23
Just before mixing boundary	1540 hrs.	N 24-49-50	E 66-57-42	47.6	13.5	NIL	-3.22
At apparent mixing boundary	1550 hrs.	N 24-49-51	E 66-57-46	49.9	20.4	>300	-6.83
Middle of Layari outfall channel	1600 hrs.	N 24-49-54	E 66-57-59	50.4	19.4	20	-5.04
Extreme of Layari outfall channel	1630 hrs.	N 24-49-53	E 66-58-06	48.4	13.6	54	-8.04
PROFILE-4 Location: In between Bhaba Island Jetty and end limit of Navel Dockyard Store, Date: 30-4-1995							
Prior to apparent mixing boundary	1630 hrs.	N 24-49-32	E 66-57-48	49.4	13.2	>300	-3.95
Prior to apparent boundary	1640 hrs.	N 24-49-32	E 66-57-53	50.6	0.8	>300	-4.7
At apparent mixing boundary	1650 hrs.	N 24-49-32	E 66-57-57	50.4	11.4	>300	-7.77
Middle of Layari outfall channel	1705 hrs	N 24-49-33	E 66-58-00	49.7	13.4	>300	-8.43
Extreme of Layari outfall channel	1715 hrs	N 24-49-33	E 66-58-05	51.4	11.2	>300	-7.43

Table-IV Physiochemical, bacteriological and stable carbon isotope analysis of lowest to highest tide water samples in Manora Channel mains (Date: 2-5-1995)

Tide Level	Collection time	E.C. (mS/cm)	Turbidity (NTU)	Total Coliform	$\delta^{13}C$ ‰ PDB
Bhit Island Jetty		**N 24-49-00 E 66-58-03**			
Highest	1230 hrs.	51.2	6.97	21	-4.03
Median	1530 hrs.	50.9	7.2	42	-4.57
Lowest	1830 hrs.	51.1	7.0	14	-7.48
Boat Club		**N 24-49-34 E 66-58-08**			
Highest	1230 hrs.	52.1	6.73	15	-4.73
Median	1530 hrs.	51.6	6.97	>300	-4.96
Lowest	1830 hrs	52	6.81	48	-5.63
Pakistan Naval Academy (PNA)		**N 24-48-03 E 66-58-24**			
Highest	1230 hrs.	51.6	7.84	NIL	-4.78
Median	1530 hrs.	51.2	7.92	7	-5.6
Lowest	1830 hrs.	50.4	7.98	>300	-6.91
Manora Lighthouse		**N 24-47-49 E 66-59-05**			
Highest	1230 hrs.	52.8	6.8	16	-3.44
Median	1530 hrs.	51.9	7.2	42	-3.69
Lowest	1830 hrs.	52.1	6.4	15	-4.53
Oyster Rocks Facing NIO		**N 24-53-34 E 66-59-56**			
Highest	1230 hrs.	52.3	5.7	NIL	-3.5
Median	1530 hrs.	51.1	5.89	46	-3.74
Lowest	1830 hrs	51.0	6.96	6.96	-3.74

Table-V Low tide $\delta^{13}C$ evolution profile tracking along south east coast of Karachi (Sep. 1997)

Time	Korangi-Phatti zone	Ibrahim Haideri (Fish Harbour)	Ghizri Creek Zone	Ghizri Mouth Zone	Clifton Casino Zone	Clifton NIO Zone
0900	-2.71	-2.29	-4.71	-1.52	-2.96	-0.91
1030	-2.75	-2.52	-5.36	-2./87	-3.72	-0.61
1200	-2.66	-2.51	-4.06	-2.87	N.D*	-0.92
1400	-2.58	-1.83	-3.08	-2.56	-2.16	-1.34
1530	-3.52	1.67	-3.56	-2.84	-2.51	-0.30
1700	-2.07	-2.03	-2.53	-2.85	-3.95	-0.60

Table-VI Low tide $\delta^{13}C$ evolution profile tracking along north west coast of Karachi (Sep. 1997)

Time	Manora Seaside Zone	Sandpit Seaside Zone	Buleji Seaside Zone	Power House Seaside Zone	Sunehry Point Zone
1000	-0.61	-0.86	-0.96	-0.70	-0.15
1200	-0.63	-1.77	-1.09	0.53	-1.59
1330	-1.63	-3.14	-0.66	-0.15	0.60
1500	-0.38	-0.41	-1.58	-1.11	-1.58
1630	-3.71	-0.63	-0.60	-1.33	-1.27
1800	N.D.*	-0.99	-0.76	-2.43	-0.85

N.D.* Not measured due to loss of sample

Table-VII $\delta^{13}C$ and $\delta^{15}N$ Composition of mangrove leaves and seaweeds in Manora Channel and along the Karachi coast.

Sample No.	Plant Type	Species Name	$\delta^{13}C$ (‰ PDB)	$\delta^{15}N$ % Air N_2
Manora Channel				
68	Sea Weeds	Ulva Spp (green)	-15.04	18.68
69	Sea Weeds	Ulva Spp (green)	-15.49	14.59
69.USP	Sea Weeds	Ulva Spp (green)	-14.31	9.73
70	Sea Weeds	Ulva Spp (green)	-15.55	9.13
71	Sea Weeds	Ulva Spp (green)	-17.29	7.84
72	Sea Weeds	Ulva Spp (green)	-13.39	N.D.
73	Sea Weeds	Ulva Spp (green)	-13.35	13.37
74	Sea Weeds	Ulva Spp (green)	-15.49	13.95
61	Mangrove	Avecinia marina	-27.85	12.28
62	Mangrove	Avecinia marina	-27.71	12.26
63	Mangrove	Avecinia marina	-26.95	10.47
64	Mangrove	Avecinia marina	-26.93	11.35
65	Mangrove	Avecinia marina	-26.72	6.18
66	Mangrove	Avecinia marina	-27.27	13.15
67	Mangrove	Avecinia marina	-27.51	8.32
		Along Coast of Karachi		
Buleji				
26	Sea Weeds	Caulerpa manorensis (green)	-15.8	10.33
27	Sea Weeds	gracilara corticata (red)	-18.73	12.08
28	Sea Weeds	Staechospermum margimum (brown)	-14.01	10.76
29	Sea Weeds	Sargasaum tennirium (brown)	-17.11	9.79
30	Sea Weeds	Sargasaum lancedotum (brown)	-17.37	11.12
31	Sea Weeds	Spathoglossum varible (brown)	-14.47	10.08
32	Sea Weeds	Scinaia indica (red)	-18.6	10.95
33	Sea Weeds	halymenia porphyroid (red)	-31.12	7.78
34	Sea Weeds	Sargassum wightii (brown)	-13.73	11.16
35	Sea Weeds	Bangia atrupupurea (red)	-17.92	10.6
36	Sea Weeds	Coelarhrum muelleri (red)	-21.63	10.29
37	Sea Weeds	Halymedatuna (green)	-9.92	10.64
38	Sea Weeds	Laurencia piatifidaar (red)	-17.82	10.75
39	Sea Weeds	Sarcodia dichotoma (red)	-19.24	11.67
40	Sea Weeds	Gelidium usmangani (red)	-15.05	8.66
41	Sea Weeds	Chaetomorpha antinnen (red)	-15.49	10.26
42	Sea Weeds	Agardhilla robusta (red)	-21.06	10.2
43	Sea Weeds	Bryopsis pinnata (green)	-13.7	11.76
44	Sea Weeds	Sarconema furcellatum (red)	-19.53	10.35
45	Sea Weeds	Utotea indica (green)	-11.57	13.73
46	Sea Weeds	Caulerpa taxifolia (green)	-14.71	11.34
47	Sea Weeds	Petalonia fascia (brown)	-13.2	8.9
48	Sea Weeds	Enteromorpha compressa (brown)	-17.82	10.11
49	Sea Weeds	Deronema abbottiae (red)	-17.28	12.03

(Table-VII continued)

50	Sea Weeds	Gracilaria follifera (red)	-13.06	11.45
77	Sea Weeds	Ulva spp. (green)	-14.93	15.54
Pacha				
1	Sea Weeds	Codiuum elongatum (green)	-13.58	15.54
2	Sea Weeds	Valoniopsis pachyneum (green)	-13.29	17.76
3	Sea Weeds	Caulepa scalpelliformis (green)	-16.05	14.01
4	Sea Weeds	Ulva fasciata (green)	-4.91	14.03
5	Sea Weeds	Cystoseira spp. (red)	-12.95	12.62
6	Sea Weeds	Jania adherence (red)	-9.49	12.08
7	Sea Weeds	botryocladia leptopoda (red)	-25	13.87
8	Sea Weeds	Codium latum (green)	-13.4	11.87
9	Sea Weeds	Colpomenia sinuosa (green)	-8.8	10.75
10	Sea Weeds	Sargassum sqarrosum (brown)	-15.11	12.22
11	Sea Weeds	Lyengaria stellata (brown)	-8.94	12.99
12	Sea Weeds	Caulerpa peltata (green)	-21.14	10.16
13	Sea Weeds	Galaxura (red)	-11.35	11.79
14	Sea Weeds	Padina tetrastromatica (red)	-16.55	14.52
15	Sea Weeds	Gracelaria pygmea (red)	-12.88	9.9
16	Sea Weeds	Padina pavonia (brown)	-10.02	9.09
17	Sea Weeds	Asparagopsis sandfordiana (red)	-19.44	13.35
18	Sea Weeds	Hypnea musciforrmis (red)	-14.69	12.57
19	Sea Weeds	Leurencia obtusa (red)	-17.41	11.57
20	Sea Weeds	Caulerpa racemosa (green)	-17.07	13.09
21	Sea Weeds	Dictyota dichoma (brown)	-15.76	12.6
Paradise Point				
22	Sea Weeds	Sargassum biveanum (brown)	-15.78	11.37
23	Sea Weeds	Champia compressa (red)	-14.68	10.94
24	Sea Weeds	Scinaia hattei (red)	-18.66	10.78
25	Sea Weeds	Hypea valentiae (red)	-15.07	10.97
78	Sea Weeds	Ulva Spp (green)	-14.87	11.39
79	Sea Weeds	Ulva Spp (green)	-14.67	9.32
Hawkes Bay				
75	Sea Weeds	Ulva Spp (green)	-14.54	10.25
76	Sea Weeds	Ulva Spp (green)	-14.08	9.75
Korangi Creek				
51	Mangrove	Avecinia marina	-28.2	9.51
52	Mangrove	Avecinia marina	-28.3	10.56
53	Mangrove	Avecinia marina	-27.57	11.4
54	Mangrove	Avecinia marina	-27.94	11.31
55	Mangrove	Avecinia marina	-27.37	7.16
54	Mangrove	Avecinia marina	-27.66	11.64
57	Mangrove	Avecinia marina	-27.88	10.79
58	Mangrove	Avecinia marina	-26.88	6.52
59	Mangrove	Avecinia marina	-27.97	7.91
60	Mangrove	Avecinia marina	-28.03	10.4

Table-VIII $\delta^{13}C$ comparison of inorganic & organic fraction of bottom sediments and water (TDIC) Karachi harbour / Manora Channel

Sample Location	Latitude/ Longitude	$\delta^{13}C$ (Inorg.) Sediment 95/96	$\delta^{3}C$ (org.) Sediment 95/96	$\delta^{13}C$ TDIC Low tide 95/96
Polluted Input Sources				
Layari River Downstream (Pre-Harbour outfall Zone)	N 24-52-27 E 67-52-01	-1.57 (-1.54)	-25.91	-9.57 (-6.89)
Malir River Downstream	N 24-49-27 E 67-05-31	N.D.	-12.77	N.D.
Layari River Outfall Area (Karachi Harbour & Manora Channel Backwaters)				
Layari River Outfall (Opposite Karachi Fish Harbour)	N 24-51-01 E 67-58-25	-2.77	-26.55	-3.41
Layari River Outfall (Shamspir Village Channel Side)	N 24-50-34 E 66-55-39	-1.25	-26.57	-8.00
Layari River Outfall (Kakkapir Village Backwaters)	N 24-50-05 E 66-55-35	-1.20	-26.40	-8.01
Layari River Outfall (Shamspir Village Backwaters)	N 24-49-50 E 66-57-27	-0.91	N.D.	N.D.
Karachi Harbour Mains				
KPT-Shipyard (Butti), Karachi Harbour /Close to Layari Outfall	N 24-49-59 E 66-58-02	-0.59	-15.46	-7.43 (-8.16)
Boat Building Area, Karachi Harbour (KPT Shipyard Channel)	N 24-50-15 E 67-07-15	-1.91	N.D.	-8.39 (-6.46)
Kaemari Fish harbour (KPT Shipyard Channel)	N 24-50-59 E 67-58-39	-4.52	-19.14	-8.01
Kaemari Boat Basin (Karachi Harbour Coast Guard Jetty)	N 24-48-58 E 66-38-30	-1.60	N.D.	N.D.
Mangrove Forest Turn Btw. Bhit Island & Shamaspir (Khi. Harbour)	N 24-51-08 E 66-55-05	-1.87 (-1.82)	-18.01	-3.40
Manora Channel Mains				
Bhit Island (Manora Channel)	N 24-49-10 E 66-58-00	-1.22 -0.56	-10.58	-3.53 -8.48
Bhaba Island (Manora Channel)	N 24-49-27 E 66-57-52	0.08 -0.24	-18.67	-5.34 -9.59
Kaemari oil Terminal (Dredged Sample, Manora Channel)		-1.57	N.D.	N.D.
Boat Club (Manora Channel)	N 24-49-27 E 66-57-52	-1.18 -1.86	N.D.	-2.62 -4.27
Pakistan Naval Academy (Manora Channel)	N 24-48-07 E 66-58-26	-0.68 -0.34	N.D.	-2.15 -3.85
Manora Lighthouse (Manora Channel)	N 24-47-33 E 66-38-54	0.64 -0.68	N.D.	-1.34 -5.61

(continued Table-VIII)

Sample Location	Latitude/ Longitude	δ^{13}C (Inorg.) Sediment 95/96	δ^{3}C (org.) Sediment 95/96	δ^{13}C TDIC Low tide 95/96
Polluted Input Sources				
Layari River Downstream (Pre-Harbour outfall Zone)	N 24-52-27 E 67-52-01	-1.57 (-1.54)	-25.91	-9.57 (-6.89)
Malir River Downstream	N 24-49-27 E 67-05-31	N.D.*	-12.77	N.D.
Manora Channel Exit	N 24-47-33 E 66-38-54	0.64 -0.68	N.D.	-1.34 -5.61
North-West Coast				
PNS Himaliya (Karachi Sea, North-West Coast)	N 24-48-30 E 66-56-29	-1.61	N.D.	-0.87
Sandspitt (Karachi Sea, North-West Coast)	N 24-49-15 E 66-55-23	-1.13	N.D.	-0.22
Kakkapir (Karachi Sea, North-West Coast)	N 24-49-55 E 66-53-55	-0.26	N.D.	-0.272
Buleji (Karachi Sea, North-West Coast)	N 24-49-04 E 66-50-41	-0.75	N.D.	-0.77
Power House South (Karachi Sea, North-West Coast)	N 24-50-13 E 67-47-56	-0.31	N.D.	-0.601
South-East Coast				
Oyster Rocks (Karachi Sea, South-East Coast, Clifton)	N 24-48-18 E 66-59-50	-1.21 -1.82	N.D.	-1.18
BTW NIO & Manora Lighthouse (Clifton Coast)	N 24-48-20 E 66-59-33	N.D.	N.D.	-2.67
BTW Oil Jetty & Oyster Rock (Clifton Coast)	N 24-48-12 E 66-59-22	-1.46	N.D.	1.89
Marina Heights-III, Clifton (Clifton Coast)	N 24-48-00 E 67-00-27	-1.39	N.D.	-1.926
Bhutto Casino, Central Clifton (Clifton Coast)	N 24-47-37 E 67-01-39	-2.16	N.D.	-0.517
BTW Marina Club & Jetty (Defense Area Coast)	N 24-46-23 E 67-03-01	-1.92	N.D.	-0.376
Gizri Coast Area	N 24-45-16 E 67-03-35	-1.2 -1.4	-7.86	-0.44 (-2.75)
Ibrahim Haideri Jungle	N 24-46-01 E 67-07-15	-1.2	-13.9	-6.06 (-0.563)
Ibrahim Haideri Fish Harbour	N 24-47-03 E 67-08-39	-2.43	-12.84	-6.97 (-1.08)
Korangi Fish Harbour		-1.31	N.D.	-1.96
Korangi- Phitti Junction		-1.05	N.D.	-0.31

N.D. Not measured

Table-IX Toxic/trace metal concentration in bottom sediments of Karachi Harbour/ Manora Channel

Sediment Sample Location	Latitude / Longitude	Collection Date/ Depth	Mn %	Cr (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Sr (ppm)	U (ppm)	V (ppm)	Zn (ppm)
Layari River Outfall Area											
Layari River Outfall (Karachi Harbour)	N 24°-51'-01" E 66°-58'-25"	29-4-95 (1.5 m)	0.03	293.00	N.D.	48.78	49.46	192.00	0.883	69.80	537.60
Layari River Outfall (Shamspir Village Channel side)	N 24°-50'-34" S 66°-55'-39"	20.-4-95 (1.2 m)	0.04	106.00	N.D.	32.40	22.41	297.00	0.975	64.80	111.40
Layari River Outfall (Kakapir Village Channel side)	N 24°-50'-05" S 66°-55'-35"	29-4-95 (1.2 m)	0.04	89.00	N.D.	36.99	21.88	339.90	0.658	60.00	85.00
Karachi Harbour Area											
KPT Shipyard (Butti) Karachi Harbour/ Close to Layari Outfall	N 24°-49'-59" S 66°-58'-02"	26-4-95 (2.5)	0.03	92.12	N.D.	1.53	18.93	449.05	1.041	45.64	83.94
Boat Building Area Karachi Harbour/ Close to Layari Outfall	N 24°-50'-21" S 66°-58'-03"	26-4-95 (3 m)	0.04	319.84	N.D.	56.46	33.84	307.77	1.660	88.26	666.28
Keamari Fish Harbour	N 24°-50'-59" S 66°-58'-39"	26-4-95 (3 m)	0.03	102.00	ND.	25.56	29.36	313.90	0.791	39.00	581.00
Manora Channel Mains											
Bhit Island	N 24°-49'-00" S 66°-58'-03"	26-4-95 (3.5)	0.05	70.00	N.D.	30.60	21.68	348.50	0.433	55.60	96.20
Bhaba Island	N 24°-49'-27" S 66°-57'-53"	26-4-95 (3.5 m)	0.04	80.00	N.D.	27.54	20.56	393.40	0.550	48.80	95.60
Keamari Oil Terminal	N 24°-48'-08" S 66°-59'-13"	26-4-95 (6 m)	0.06	82.00	N.D.	39.06	23.71	262.20	0.408	67.80	524.00
Light House (Manora Channel Inner Exit)	N 24°-47'-33" S 66°-58'-54"	26-4-95 (6.9 m)	0.03	14.00	N.D.	7.04	9.00	581.30	0.383	15.80	15.60

N.D. Not measured

Table-X Toxic/trace metal concentration in bottom sediments along the coast of Karachi.

Sediment Sample Location	Latitude / Longitude	Collection Date/ Depth	Mn %	Cd (ppm)	Cr (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Sr (ppm)	U (ppm)	V (ppm)	Zn (ppm)
Karachi Sea South East Coast												
Btw. Oil Jetty/ Oyster Rocks (Clifton Coast)	N 24°-48'-12" S 66°-59'-22"	29-4--95 (3.5 m)	0.09	N.D.	85.00	N.D.	58.86	27.03	193.10	0.241	118.20	161.00
Bhutto Casino) (Clifton Coast)	N 24°-47'-32" S 67°-01'-39"	29-4--95 (4.5 m)	N.D.	0.21	33.01	16.09	46.06	22.4	N.D.	N.D.	N.D.	73.2
Naval Jetty (Clifton Coast)	N 24°-47'-04" S 67°-03'-01"	29-4--95 (7.5 m)	N.D.	0.14	25.79	13.41	43.37	19.12	N.D.	N.D.	N.D.	51.9
Btw Marina Club & Naval Jetty (Defence Coast)	N 24°-46'-23" S 67°-03'-01"	29-4--95 (6.4 m)	N.D.	0.11	26.54	13.49	46.46	10.61	N.D.	N.D.	N.D.	59.5
Ghizri Coast	N 24°-45'-23" S 67°-03'-39"	17-1-96 (7.4 m)	0.04	 0.09	12.00 12.5	 6.75	18.80 27.5	16.94 21.15	217.80	0.283	41.80	41.40 36.5
Manora Channel Exit												
Btw. NIO & Manora Lighthouse (Clifton Coast)	N 24°-48'-20" S 66°-59'-33"	29-4--95 (3.5 m)	0.05	N.D.	70.00	N.D.	43.65	22.92	216.00	0.191	97.60	119.60
Btw. Oil Jetty/ Oyster Rocks (Clifton Coast)	N 24°-48'-12" S 66°-59'-22"	29-4--95 (3.5 m)	0.09	N.D.	85.00	N.D.	58.86	27.03	193.10	0.241	118.20	161.00
Light House Manora Exit	N 24°-47'-53" S 66°-59'-04"	29-4--95 (3.5 m)	N.D.	0.18	19.23	18.56	38.46	21.15	N.D.	N.D.	N.D.	48.68
Karachi Sea North West Coast												
PNS Himaliya	N 24°-48'-30" S 66°-56'-29"	16-1-96 (8.3 m)	N.D.	0.08	23.69	15.63	37.91	21.5	N.D.	N.D.	N.D.	49.25
Sandspit (Karachi Coast, North West Coast)	N 24°-49'-15" S 66°-55'-23"	16-1-96 (7.3 m)	0.04 N.D.	N.D. 0.11	33.00 15.0	N.D. 8.25	23.94 35.0	15.42 15	325.00 N.D.	0.408 N.D.	49.60 N..D.	49.80 32.0
Buleji (Karachi Coast, North West Coast)	N 24°-49'-04" S 66°-50'-41"	16-1-96 (8.3 m)	0.06 N.D	N.D. 0.15	80.00 25.5	N.D. 20.04	38.13 37.6	25.10 17.91	375.30 N.D.	0.358 N.D	88.50 N.D.	80.40 45.8
Kakka pir (Karachi Coast, North West Coast)	N 24°-49'-55" S 66°-53'-55"	16-1-96 (9.6 m)	N.D.	0.10	18.18	8.78	36.66	17.71	N.D.	N.D.	N.D.	29.05
Power House (Karachi Coast, North West Coast)	N 24°-50'-12" S 66°-47'-56"	16-1-96 (5.8 m)	0.13	N.D.	20.00	N.D.	12.48	25.10	--	0.95	36.80	80.40

N.D. Not measured

0.81 ‰ during high tide condition and -0.61 to -0.82 ‰ during low tide conditions. There is also some suggestion of Layari River pollution input in Paradise Point area due to a circular movement of polluted breakwaters off Manora Channel. These results indicate that North-West coast of Karachi is much less polluted as compared to South-East Coast. This is due to the fact that North-West coast is not highly populated and industrialized. Also, pollution load of small villages on North-West coast is mostly drained to backwaters of Manora Channel except for a small strip near Paradise point. Tables-VI present results of time evolution of pollution mixing trends at various locations along the northwest coast during mid low to mid high tide regime. It appears that pollution levels at Manora seaside station, Sandspit seaside station and power house station start increasing after a shift from lowest tide to highest tide regime, thereby indicating influx of pollution from breakwater zone off Manora Channel exit. Occasional high shifts in the Buleji Seaside station are attributed to sudden input of waste from Buleji Village.

3.2 Sea plants pollution profile

3.2.1 ***Mangrove pollution:*** Table-VII presents the stable carbon isotope composition of mangroves (Avecinia Marina) leafs and seaweed samples (mainly species of Ulva). The $\delta^{13}C$ values of mangroves in the backwaters of Manora Channel range between -26.7 to -27.9 ‰ PDB and are quite in agreement with $\delta^{13}C$ values quoted in literature for the tropical mangroves in Malaysia [10]. However, Mangroves in the polluted Korangi Creek industrial area (facing open sea) are more depleted in ^{13}C (range: -26.9 to -28.3 ‰ PDB) as compared to Backwaters of Sandspit area. This depletion is attributed to high inputs of industrial waste related organic chemicals in Korangi Creek area. These $\delta^{13}C$ values will serve as reference to identify future inputs of pollution in mangrove growth areas along the coast of Karachi. $\delta^{15}N$ values of mangroves in the Manora Channel range between +6.2 ‰ to +13.2 ‰ air N_2 and are quite comparable with values for the Korangi Industrial area Creek Mangroves (+6.5 ‰ air N_2 to +11.6 ‰ air N_2.). These values suggests biological fixation of Nitrogen from manure/wastes deposited by Layari river and its tributaries in Manora Channel Backwaters as the $\delta^{15}N$ values of NH_4^+ & NO_3^- in manure/domestic waste range between +14 to + 17.3 ‰ air N_2 and +11 to +38.4 ‰ air N_2 [9].

3.2.2 ***Seaweed pollution*****:** In Manora Channel, $\delta^{13}C$ values of seaweeds (mainly species of Ulva) lie in the range from -13.35 ‰ PDB to -17.29 ‰ PDB. A trend towards more negative $\delta^{13}C$ values indicates impact of pollution in their respective growth areas. In case of northwest coast, $\delta^{13}C$ values of seaweed (mainly species of *Ulva*) lie in the range from -4.9 ‰ PDB to -31.1 ‰ PDB (Table-VII). Large variations in $\delta^{13}C$ of seaweeds in Buleji and Pacha areas suggest incorporation of carbon from the domestic/industrial sources. Like mangroves, $\delta^{15}N$ values of seaweeds pertaining to Manora Channel & the inshore off northeast coast range between +7.84 ‰ to +18.68 ‰ air N_2 and suggest biological fixation of Nitrogen from manure/wastes deposited by Layari river and its tributaries in Manora Channel Backwaters and sewage drains in Buleji and Pacha areas along the northwest coast.

3.3 Sea bottom sediment pollution

3.3.1 ***Carbon Isotope Composition*****:** Sediments pertaining to Manora Channel are fine sands with appreciable amounts of clayey fraction and micaceous minerals. The organic carbon in the sediments ranges around 0.45 %. The higher carbon contents are found in sediments of Karachi Harbour and Layari River outfall zone. Table-VIII shows a comparison of $\delta^{13}C$

values of sea bottom sediments and water samples in the study area. Clearly the inorganic $\delta^{13}C$ values of sediments are typical of marine shells and carbonate minerals. However, it is evident that relatively more depleted $\delta^{13}C$ values ranging between -1.25 to -4.52 ‰ PDB for inorganic carbon and -15.9 to -26.6 ‰ PDB for organic carbon are found in the Layari River outfall and the Karachi Harbour zone. The Manora Channel Mains has relatively enriched $\delta^{13}C$ values ranging between -0.34 to -1.86 ‰ PDB for inorganic carbon to -10.58 to -18.67 ‰ PDB. In this zone, more negative values of inorganic carbon are found in the zone between Bhit Island and Boat Club. Although more data related to organic carbon of sediments is yet awaited, it is clear that the entire harbour bottom sediments are polluted with organic waste derived from mangrove forests and the Layari River outfall zone.

Sediments pertaining to the northwest coast are more silty and contain fine to coarse sand with about 20 % calcium carbonate content. In contrast, sediments pertaining to Manora Channel exit and the south-east coast are fine sands with appreciable amounts of micaceous minerals, clayey fraction and comparatively low calcium carbonate content of about 10 %. The organic carbon in the sediments range between 0.24 % to 0.45 %. The higher carbon contents are found in in-shore sediments of southeast coast and the Manora channel exit. Table-V-III shows a comparison of inorganic and organic $\delta^{13}C$ values of sea bottom sediments and water samples in the study area. $\delta^{13}C$ values of Layari River downstream are in the range of -1.5 ‰ PDB for inorganic carbon and -25.9 ‰ PDB for the organic carbon. Along the coast, inorganic $\delta^{13}C$ values ranging between -0.3 to -2.43 ‰ PDB are typical of marine shells and carbonate minerals. Relatively more depleted inorganic $\delta^{13}C$ values ranging between (-1.05 to -2.43 ‰ PDB) are found in the sediments of southeast coast as compared to the northwest coast (-0.26 to -1.61 ‰ PDB). In the southeast, coastal sediments closer to the local waste drains are more depleted (-2.16 ‰ PDB near Bhutto Casino zone, -2.43 ‰ PDB near Ibrahim Haideri Fish Harbour). This is also reflected in the significantly depleted $\delta^{13}C$ values around -13 ‰ PDB. The input sources mainly, the Manora Channel exit has relatively enriched inorganic $\delta^{13}C$ values ranging between -0.34 to -1.86 ‰ PDB. Along the northwest coast, the Manora Island zone is characterized by relatively more depleted values of inorganic $\delta^{13}C$ values around -1 ‰ PDB. The remaining coast has inorganic ^{13}C values mostly below 0.3 ‰ PDB. This also shows that this part of Karachi sea is relatively least polluted.

3.3.2. Trace element analysis of sediments: Table-IX presents the minor & trace element concentrations in shallow sea bottom sediments in Manora Channel. It may be noted that significantly high average concentrations of Cr (89-319 ppm), Ni (1.5-56 ppm), Pb (9-49ppm), V (15-69 ppm) and Zn (15 - 581 ppm) are found in the Layari River outfall and Karachi Harbour zone. Similar concentrations of Cr (29-336 ppm), Ni (29-51 ppm), Pb (16-56 ppm) and Zn (71-170 ppm) have been found by the National Institute of Oceanography (NIO)-Karachi, in four samples of the Karachi Harbour area [3]. Karachi harbour is found to be the most polluted zone whereas, the Manora Channel Mains is relatively less polluted zone. These values are quite in agreement with the results obtained from $\delta^{13}C_{TDIC}$ composition. The presence of high concentration of these toxic metals in Harbour sediments is attributed to input of industrial waste effluents related to leather tanning industries, electroplating industries, battery material, waste from Karachi shipyard & Naval dockyard into the Karachi harbour area. For a small scale study in the Korangi-Phitti Creek, IAEA-Marine Environment Laboratory (Monaco) has reported concentrations of: Cr in the range of 2-19 ppm, Ni in the range of 3-7 ppm, Pb in the range of 3-13 ppm and V in the range of 4-13 ppm [1]. Concentrations of uranium (U) in Karachi sea sediments are not high. However, contents of U in sediments pertaining to Layari River mouth area and Karachi Harbour area are higher as compared to sediments collected from Manora Channel entrance and areas facing open sea. Similar concentrations of Cr, Ni, Pb, V and Zn have been reported in the literature for Oman Harbour, Kuwait Harbour, Bahrain Harbour and Bombay Harbour [11].

Table-X presents trace element concentrations in selective shallow sea bottom sediments of Karachi Sea Southeast coast, Manora Channel exit and the northwest coast. It may be noted that significantly high average concentrations of Cr (12-85 ppm), Ni (18-58 ppm), Cu (6-16 ppm), Pb (10.6-27 ppm), Cd (0.09-0.21 ppm), U (0.241-0.283 ppm), Sr (193-217 ppm), V(42-118 ppm) and Zn (41.-161 ppm) are found in the Manora Channel Exit zone. Similar concentrations of Cr (20-26 ppm), Ni (35-42 ppm), Pb (19-21 ppm), Cu (11-17 ppm), Cd (0.14-0.215 ppm) and Zn (ppm) have been reported by the National Institute of Oceanography (NIO)-Karachi, in coastal sediments off Karachi [3, 11, M. Saleem, National Institute of Oceanography, unpublished data, personal communication]. The sediments pertaining to the southeast coast off Karachi have relatively high concentrations of these toxic elements except (Sr, U) as compared to the northwest coast. For a small scale study in the Korangi-Phitti Creek, IAEA-Marine Environment Laboratory (Monaco) has reported concentrations of: Cr in the range of 2-19 ppm, Ni in the range of 3-7 ppm, Pb in the range of 3-13 ppm and V in the range of 4-13 ppm [1]. Concentrations of uranium (U) in Karachi sea sediments are not high. However, contents of U in sediments pertaining to Layari River mouth area and Karachi Harbour area are higher as compared to sediments collected from Manora Channel entrance and areas facing open sea. The high concentrations of toxicity in sediments of southeast coast of Karachi are due to several factors. Firstly, Korangi-Phitti creek on southeast coast mostly receives domestic sewage, agrochemical wastes, industrial waste waters etc. Secondly, sediments along this coast have high contents of clayey matter which have in-turn high absorption or trapping capacity for metals. Thirdly, this distribution is due to impact of monsoons. During the winter (October - February), the northwest monsoon winds are relatively weaker, resulting in diminishing upwellings. The seawater from the nearshore and off-shore Indus Delta enters the coastal waters of Karachi from the southeast and moves along the coast towards the northwest or westwards and then to the western coast of Karachi. Thus, it moves in the southwest direction to the offshore area. During this type of a circulation pattern in the open sea, small clockwise gyres are developed along the beach. During the southwest monsoon (May - September), the dominant direction of seawater flow in the coastal waters of Karachi remains clockwise, i.e. the major flux of seawater from the offshore area enters the coastal waters of Karachi at the western part of the coast from the southwest direction. During this type of a circulation pattern in the open sea, small anti-clockwise gyres are developed along the beach. Due to weak speed of water in the winter monsoon and the south-west direction water movement in the summer monsoon, the contaminated water plume is not effectively spread in the direction of northwest coast. Thus metal rich water accumulates in the sediments of southeast coast and the Manora channel exit zone.

4. CONCLUSIONS AND RECOMMENDATIONS

The present results clearly indicate that the inshore shallow sea waters off Karachi coast are being continuously polluted by input of unplanned and untreated disposal of industrial and domestic waste water into the Karachi sea via Layari River outfall. The physiochemical and bacteriological analysis have given a rough evaluation of the aerial extent of the polluted zone in the Karachi harbour area and the Manora Channel Mains in response to mixing of Layari River water with the Arabian Sea water under high and low tide conditions. The mangrove ecosystem seems to play an important role in controlling the level of contamination in the Layari River outfall zone and the Karachi Harbour area in response to high tidal fluctuations. Nevertheless, the severity of pollution inventory decreases as we move out of Bhaba/Bhit islands towards the Manora Channel exit (open sea zone). This pollution is also reflected in the stable isotope composition of carbon (^{13}C) in TDIC pool, organic carbon in bottom sediments, mangrove leaves and seaweeds grown in the Layari River outfall area and the Manora Channel backwaters area. Some general conclusions and recommendations drawn from this study are as following:

(1) Environmental stable isotope techniques may be used as dynamic pollution indicators of coastal marine environments.

(2) Tidal fluctuations and monsoons play a key role in controlling the distribution of contamination inventories in shallow sea water off Karachi coast.

(3) Manora channel is the most polluted zone along the coast of Karachi, both during high and low tidal conditions.

(4) The southeast coast of Karachi is significantly polluted during low tide conditions since it receives polluted waters from Manora channel exit as well as from Malir river (Ghizri creek) and Korangi creek.

(5) The northwest coast of Karachi is least affected by polluted waters of Manora channel.

(6) Stable carbon and nitrogen isotope composition of sea plant leafs and sediments also reflect pollution inventories from industrial and domestic sources.

(7) The concentrations of toxic metals such as Pb, Ni, Cr, Zn, V are quite significant in sediments of Karachi harbour area Manora channel exit & Oyster rock zone due to input of industrial wastes/effluents into the harbour area via Layari river and transport of contaminated sediments from the southeast coast due to impact of monsoons.

(8) The continuous pollution inventories along the coast of Karachi will have adverse effects in terms of (i) increase in toxicity levels of marine food chain; (ii) considerable stress on fish habitat and mangroves; (iii) corrosion of cargo ships and navel vessels; and (iv) significant ill effects on the health of bathing tourists and inhabitants of Bhaba & Bhit islands, naval dockyard and Manora channel.

Immediate remedial actions are required to combat pollution inventories in the Manora channel-Karachi harbour area & other contaminated zones along the coast of Karachi. It is recommended that:

(1) All industrial units in Karachi must treat waste effluents prior to discharge into Layari river, Malir river, Gizri creek, Korangi creek or large volume local waste drains.

(2) Waste treatment plants should be installed downstream of Layari river and Malir river to eliminate pollution in the Karachi harbour and inshore waters off southeast coast of Karachi.

(3) More studies are required to track record of pollution inventories, areal distribution of pollutants and their impact on the marine food web and mangrove forests etc.

ACKNOWLEDGEMENTS

Dr. Riffat M. Qureshi is thankful to IAEA for providing financial assistance for this study under IAEA - Research Contract PAK-8127. Kind support, guidance and coordination provided by Mrs. Jane Gerardo-Abaya (Technical Officer, Section *of Isotope Hydrology, IAEA) during various phases of this study is highly appreciated. The authors wish to acknowledge Dr. Shahid Amjad (National Institute of Oceanography, Karachi) for provision of necessary facilities at NIO during execution of field work. Analytical assistance provided by (i) Mr. Zahid Latif for stable isotope analysis at RIAD/PINSTECH, (ii) Mrs. Farhat Waqar & Mrs. Saida Jan (NMD/PINSTECH) for ICP-EOS toxic metal analysis of sediment samples is highly acknowledged. Thanks are also due to Mr. Sikander Ali (PSO, NIBGE, Faisalabad) for determination of Total Kjeldahl Nitrogen.*

REFERENCES

[1] MARINE POLLUTION BASELINE SURVEY IN THE KORANGI - PHITTI CREEK, PAKISTAN. Final Report of the IUCN Contract NO. OD/CDC/201/IAEA - Pakistan Baseline Survey, Project 9128. Prepared by the IAEA-Marine Environmental Studies Laboratory, International Laboratory of Marine Radioactivity, IAEA Oceanographic Museum, MC 98000, Monaco (November, 1987).

[2] ALI, I; S. Jilani. Study of contamination in the coastal waters of Karachi. In: THE ARABIAN SEA, Living Marine Resources and the Environment (eds. M. F. Thompson, N. M. Tirmizi), Vanguard Books (Pvt) Ltd., 45 The Mall, Lahore, Pakistan (1995) 653-658.

[3] KHAN, S. H., M. SALEEM., A preliminary study of pollution in Karachi harbour. In: Marine Science of the Arabian Sea. (eds. M. F. Thompson, N. M. Tirmizi), American Institute of Biological Sciences, Washington D. C. (1988) 539-547..

[4] AHMED, M. An assessment of the magnitude of coastal pollution in Pakistan through a study of its fauna and fisheries. Thalassia Juglosl, 13, pp: 395-412 (1977).

[5] QURAISHEE, G.S. Influence of the Indus River on the marine environment. In: International Conference on the Management of the Environment. pp: 111-112. Pakistan Academy of Sciences, Islamabad.

[6] KHAN, A.A., Monsoon changes and paleoproductivity in Northwestern Arabian Sea sediments. In: THE ARABIAN SEA, Living Marine Resources and the Environment (eds. M. F. Thompson, N. M. Tirmizi), Vanguard Books (Pvt) Ltd., 45 The Mall, Lahore, Pakistan (1995) 587 - 598.

[7] RIZVI, S.H.N.; T.M.A. KHAN; S.M. ALI; J. BAQUER. Circulation patterns in the Karachi coastal waters in relation to the outfalls. In: THE ARABIAN SEA, Living Marine Resources and the Environment (eds. M. F. Thompson, N. M. Tirmizi), Vanguard Books (Pvt) Ltd., 45 The Mall, Lahore, Pakistan (1995) 641-652.

[8] GUIDEBOOK ON NUCLEAR TECHNIQUES IN HYDROLOGY, Technical Report Series No. 91 (1983 Edition), International Atomic Energy Agency (IAEA), Vienna, Austria (1983).

[9] FRITZ, P., J. C. FONTES (Eds.), Handbook of Environmental Isotope Geochemistry, Vol. I, Vol. II, Elsevier, New York (1980).

[10] RODELLI, M. R., J. N. GEARING, P.J. GEARING, N. MARSHALL, A. SASEKUMAR, Stable isotope ratios as a tracer of mangrove carbon in Malaysian ecosystems", Oecologia (Berlin), 61 (1984) pp:326-333.

[11] SALEEM, M., G. N. QAZI, Distribution of trace metals in the sea-water and surficial sediment of the Karachi harbour. In: THE ARABIAN SEA, Living Marine Resources and the Environment (eds. M. F. Thompson, N. M. Tirmizi), Vanguard Books (Pvt) Ltd., 45 The Mall, Lahore, Pakistan (1995) 659 - 666.