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STABLE CARBON ISOTOPE RATIO ($\delta^{13}C$) OF SHALLOW MARINE BOTTOM SEDIMENT AS EVIDENCE OF POLLUTION IN MANORA CHANNEL, KARACHI, PAKISTAN

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Marine sediments are one of the endpoints for domestic /industrial contaminants from land based sources and provide an archive for tracing pollution record. Contaminated sediment is a significant environmental problem affecting many marine ecosystem. In the present study sediment samples from Manora Channel/Karachi harbour were analyzed for stable isotope composition of inorganic and organic carbon fractions (measured as $\delta^{13}C$) to estimate the land based terrestrial organic matter in the Manora Channel. The principle of this application lies in the fact that $\delta^{13}C$ values of inorganic carbon (mineral fractions such as calcite, aragonite, dolomite) differs vastly from that of the organic carbon fraction of domestic and/or industrial origin in the sediments. Relatively more depleted $\delta^{13}C$ (organic) values ranging between - 30.65 to -19.27 ‰ PDB for the organic carbon fraction were found in the Layari river outfall zone. In Manora channel mains enriched values $\delta^{13}C$ was found in sediment of Manora lighthouse (-5.0 ‰ PDB) and Pakistan Naval Academy (-11.76 ‰ PDB) while in same zones depleted values of $\delta^{13}C$ was found in Bhabba island (-27.31‰ PDB), Bhit Island (-26.13‰ PDB) and Boat Club area (-23.08‰ PDB) indicating impact of domestic sewage added to the Manora channel from surrounding Islands. $\delta^{13}C$ (inorganic) fraction of sediment follow similar trend. In conclusion, this study indicates that the bottom sediments of Karachi Harbour and Layari river outfall zones are mainly polluted with organic waste of domestic origin derived from Layari river.

Keywords: Stable Isotope, Carbon, Oxygen, DIC, Pollution, Karachi, Manora

1 Introduction

The ratio of carbon isotopes ($^{13}C/^{12}C$) can be used to trace carbon in the environment with natural abundance [1-3]. In coastal waters, the amount of terrigenous organic carbon (TC) in sediment is expected to decrease with increasing distance from the source(s) of pollution source and with a corresponding increase in marine organic carbon (MC) [4]. The $\delta^{13}C$ value of the sediment organic carbon reflects the proportions of TC and MC: sediments with a higher proportion of TC will have relatively low $\delta^{13}C$ and sediments with a higher proportion of MC will have relatively high $\delta^{13}C$ [5]. The isotopic composition of dissolved inorganic carbon (DIC) is a sensitive tracer of the oxidation of organic matter within sediments because the $\delta^{13}C$ value of sedimentary organic matter is much less than that of bottom water DIC and $CaCO_3$.

Several techniques are used to determine the pollution extent in the coastal sediment. The most commonly used physico-chemical techniques involve measurement of nutrients, pesticides and toxic/trace metals in the sea matrix. However, more reliable and precise techniques are the nuclear techniques which involve measurement of environmental stable isotope ratios of oxygen, carbon, sulfur and nitrogen.

The aim of this investigation was to address the feasibility of utilizing the stable carbon isotope signature in marine sediment to establish relationship between pollution and carbon isotope.

2. Description of Study Area

Karachi is located on the northern boundary of the Arabian Sea. It is the largest city of Pakistan with coastline extending upto about 30 km. The domestic waste generated by a population of ~10

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million and industrial waste generated by more than 1000 large industrial units (chemical industry, textile industry, leather tanning industry, fish processing industry, cement industry, steel mills, thermal power plants, oil refineries etc.) is drained into Karachi sea mainly via Layari River, Malir River and Korangi Creek . Maximum waste is discharged into the sea by Layari River via Manora Channel/Karachi Harbour. 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 [6-9]

Manora Channel is a navigational channel. It connects the Karachi port with the Arabian Sea in the south.It spreads over an area of 7.17 km^2 and includes the Karachi Harbour and the Kamari 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 addition of sediments in the Karachi harbour area is mainly brought by the Layari which flows through the Karachi East, falls into the sea through backwaters of the Manora Channel and Sandspit [10]. It 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, detergents, waste farm-wood, processing plants (mainly fish), 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. The quantity of domestic wastes produced per household in Karachi varies from 100 to 280 liters per day [11]. The abiological and biological dissolution of organic matter in bottom sediments of Manora channel also add to the deterioration of water in the channel. Also 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 (which supply oil to the north of the country) at harbour is responsible for the discharge of the washings alongwith all contaminants which ultimately enter the sea. Liquid wastes and effluents from fish market and fish processing plants at the fish harbour also discharge their wastes directly into the Manora channel. Manora Channel also receives untreated domestic wastes from five villages, namely the island of Manora, Bhaba Island, Bhit Island, Shams Pir and Kakka Pir.

3. Sampling and Analysis

Sediments samples were collected from: (i) Layari River out fall area, (ii) Karachi Harbour Area (iii) Manora Channel Mains during Feb 2007 (Figure 1). Samples were collected during the low tide period using conventional mechanized tourist using conventional Peterson Grab. Samples were contained in high quality polythene bags. From each zone more than one samples were collected depending upon the area. Detail of sampling point in each zone is given in Table 1.

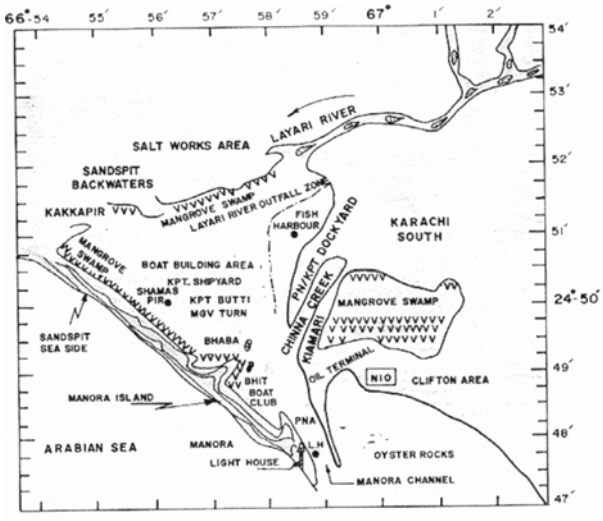

Figure 1. Coastal map of Manora channel showing sampling points

In the laboratory the samples were freeze dried and sieved through 60 mesh sieve prior to analysis.

3.1 Laboratory Analysis

3.1.1 ^{13}C Inorganic Fraction

20-25 mg sediment samples were reacted with Reagent Grade H_3 PO_4 (85%) in a vacuum line to evolve CO_2. The evolved CO_2 gas and moisture were condensed in a trap held at liquid nitrogen temperature (-196 ^oC). The temperature of the

Table 1. Sampling points in different zones in Manora Channel.

S. No	Sampling Area	Sampling points
1	Layari River Outfall Area	of Layari River, Layari River Outfall, Layari River Outfall Mangrove Area, Layari Mouth, & Sandspit Channel side
2	Karachi Harbour Area	Karachi Port Trust, Boat Building Area and Keamari Fish Harbour.
3	Manora Channel Mains	Bhabba Island, Boat Club, PNA, Manora Lighthouse, Oil Jetty, Kaemari Oil Terminal
4	Manora Channel Exit	Oyster Rock, Between NIO & Lighthouse, Between Oyster & Oil Jetty

distillation trap was then raised to - 70 ^{o}C with the help of liquid nitrogen- Freon mixture in order to transfer the CO_2 in a suitable sample collector for mass spectrometric analysis. The CO_2 was purified of water vapour and traces of air then analyzed by mass spectrometer to measure the $^{13}C/^{12}C$ ratios relative to Laboratory Carbonate Standard [12].

3.1.2 ^{13}C Organic Fraction

For preparation of CO_2 gas from sediments, about 20 - 25 mg moisture-free powdered (60 mesh) sample was placed in a porcelain boat (8 cm x 1 cm x 0.8 cm) and introduced into the quartz portion of the vacuum system. After preliminary evacuation (10^{-2} torr), high purity oxygen was filled in the combustion part of the line at pressure slightly less than one atmosphere. The sample boat was externally heated with a gas burner (~600 ^{o}C). The evolved CO/CO_2 were then circulated in the line with the help of a magnetically driven circulation pump. During this circulation, CO_2 gas and moisture was condensed in a trap held at liquid nitrogen temperature (-196 ^{o}C). The CO gas was converted to CO_2 by passing over the heated copper gauze (900 ^{o}C) in the presence of oxygen. After 5 minutes of circulation, all CO was converted to CO_2 and collected totally in the CO_2 trap. The temperature of this trap was then raised to -70 ^{o}C with the help of liquid nitrogen-feron mixture in order to transfer the CO_2 in a suitable sample collector for mass spectrometric analysis [12]. The stable carbon isotope data is expressed as δ‰ (delta per mill.) values relative to the international carbonate standard PDB (Pee-Dee Belemnite). The reproducibility of $\delta^{13}C$ measurements was better than 0.1 ‰ for working standards.

4. Results and Discussion

Stable carbon isotopic values of $\delta^{13}C$ inorganic and organic fraction in shallow sea bottom sediments in Layari river outfall zone, Karachi harbour area, Manora channel main and Manora channel exit are shown in Table 2. Results are discussed in the following section:

4.1 Layari River Outfall Area

Layari River outfall area comprises of Layari River, Layari River Outfall, Layari River Outfall Mangrove Area, Layari Mouth, and Sandspit Channel side. $\delta^{13}C_{(organic)}$ values in the Layari River outfall area vary from -19.27 to –30.65 per mill PDB and $\delta^{13}C_{(inorganic)}$. vary from –1.33 to –2.86 per mill PDB. An abrupt decrease in $\delta^{13}C_{org}$ values was recorded in the sediment of Layari River outfall Mangrove area (-30.65 per mill PDB). The pollution load of organic matter in Layari River out fall zone is attributed due to untreated terrestrial domestic waste which is drained through Layari river.

4.2 Karachi Harbour Area

Karachi Harbour area comprises of Karachi Port Trust, Boat Building Area and Keamari Fish Harbour. This area also accumulates organic particulates in sediment carried from Layari. Depleted $\delta^{13}C_{(organic)}$ values are observed throughout Karachi Harbour zone (-29.62 to -23.04 per mill PDB). These high negative values of $\delta^{13}C_{(organic)}$ indicate input of domestic waste in the area. $\delta^{13}C_{(inorganic)}$ ranges from –2.81 to –1.87 per mill PDB which also show similar pattern of pollution load in sediment.

Table 2. Stable carbon isotope composition of shallow marine bottom sediment samples of Manora channel/Karachi harbour

S. No.	Code	Location	$\delta^{13}C$ (Organic)	$\delta^{13}C$ (Inorganic)
Layari River outfall Area				
1	55	Layari River	-19.27	-1.89
2	1	Layari River Outfall	- 21.40	-1.60
3	40	Layari River Outfall Mangrove Area	-30.65	-2.86
4	12	Layari Mouth	-24.96	-1.33
5	18	Sandspit Channel	-28.18	-2.8
Karachi Harbour				
1	53	KPT Shipyard	-29.62	-2.81
2	10	Boat Building Area	-26.95	-2.10
3	11	Fish Harbour	-23.04	-1.90
4	22	Mangrove Turn	-23.23	-1.87
Manora Channel Main				
1	39	Bhaba Island	-27.31	-2.18
2	37	Bhit Island	-26.13	-2.10
3	4	Boat Club	-23.08	-1.97
4	5	PNA	-11.76	-0.68
5	6	Manora Lighthouse	-5.00	-0.64
6	15	Oil Jetty	N.D*.	-1.46
7	8	Oil Terminal	-17.94	-1.87
Manora Channel Exit				
1	7	Oyster Rock	N.D.	-1.01
2	13	Btw NIO & Lighthouse	-13.99	-1.20
3	14	Btw Oyster & Oil Jetty	-10.90	-1.49

*N.D. Not detected

4.3 Manora Channel Main

Bhabba Island, Boat Club, PNA, Manora Lighthouse, Oil Jetty, Kaemari Oil Terminal are main location in Manora Channel Mains. $\delta^{13}C_{(organic)}$ values start to decrease as further away from Layari river mouth and reach their lowest value (- 5.0 per mill) in sediment pertaining to Manora Lighthouse which clearly showed the impact of Layari river waste in this area. Similarly, Pakistan Naval Academy which is next to Manora Light facing toward Layari outfall area has $\delta^{13}C_{(organic)}$ value -11.76 per mill PDB and Bhabba and Bhit island which are in vicinity of Layari river outfall zone has more depleted values. $\delta^{13}C_{(inorganic)}$ values ranges from – 2.18 to –0.64 per mill PDB. The results in this zone clearly indicate that polluted sites have much depleted $\delta^{13}C$ organic values.

4.4 Manora Channel Exit

Oyster Rock, Between NIO & Lighthouse, Between Oyster and Oil Jetty comprises Manora channel exit zone. In sediment collected near Oyster rocks, $\delta^{13}C$ organic was not detected which is indicative of negligible organic matter in this area. While $\delta^{13}C$ in the sediment between NIO and Manora lighthouse and between Oyster rocks and Oil Jetty were –13.99 and –10.90 per mill PDB respectively showing very less impact of land based terrestrial pollution in the area.

5. Discussion

Stable carbon isotopes, which are widely used to determine the sources of organic matter in aquatic food webs [13] had previously been shown to be useful in sediment [14] This approach makes use of the fact that different biochemical pathways and the degree to which carbon (and nitrogen) has been reworked, will lead to different ratios of ^{13}C and ^{12}C. When the resulting stable isotope signatures of the different sources (so-called “end members”) are sufficiently different, it is possible to apportion the sources of organic matter.

Sediments pertaining to Manora Channel are fine sands with appreciable amounts of clayey fraction and micaceous minerals. The $\delta^{13}C$ values of organic matter in the sediments show a range of values from terrestrial (-28.5 per mill PDB) to mixed aquatic terrestrial (-24 per mill PDB). A range of phytoplankton values have been reported in the the range of -13 to -19 per mill PDB by Descolas-Gros and Fontugne [15].

Sediments containing mostly marine (phytoplankton-dominated) organic matter typically give $\delta^{13}C$ values of -19 to-21 per mill PDB. [13]. Polluted sites have different carbon isotope composition as compared to unpolluted sites. The polluted locations which receives domestic wastes have $\delta^{13}C$ (organic) values around –25 per mill PDB, while less polluted site have enriched values of $\delta^{13}C$ (organic). 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 -2.86 to -1.33 per mill PDB for inorganic carbon and -30.6 to -19.27 per mill PDB for organic carbon are found in the Layari River outfall and Karachi Harbour zone. The Manora Channel Mains has relatively enriched $\delta^{13}C$ values ranging between -2.18 to -0.64 per mill PDB for inorganic carbon to -27.31 to –5.0 per mill PDB. In this zone, more negative values of inorganic carbon are found in the zone between Bhit Island and Boat Club it is clear that the entire harbour bottom sediments are polluted with organic waste derived from mangrove forests and the Layari River outfall zone. The Karachi Harbour area receives domestic, agricultural and industrial wastes.

The high values of $\delta^{13}C$ values in sediments of Karachi harbour are due to several factors. Firstly, it mostly receives domestic sewage, agrochemical wastes, industrial waste waters etc. Secondly, sediments along this coast have high contents of clay matter which have in-turn high absorption or trapping capacity for organic matter. Fig. 2 shows values $\delta^{13}C$ organic in the studied area. From the figure it is clear that most sites near to pollution source (Layari River) are relatively more polluted as compared to other areas. Over the last decade, chemical and domestic waste contamination of sediments has been recognized as a serious problem in coastal waters. Other adverse economic impacts of contaminated sediments

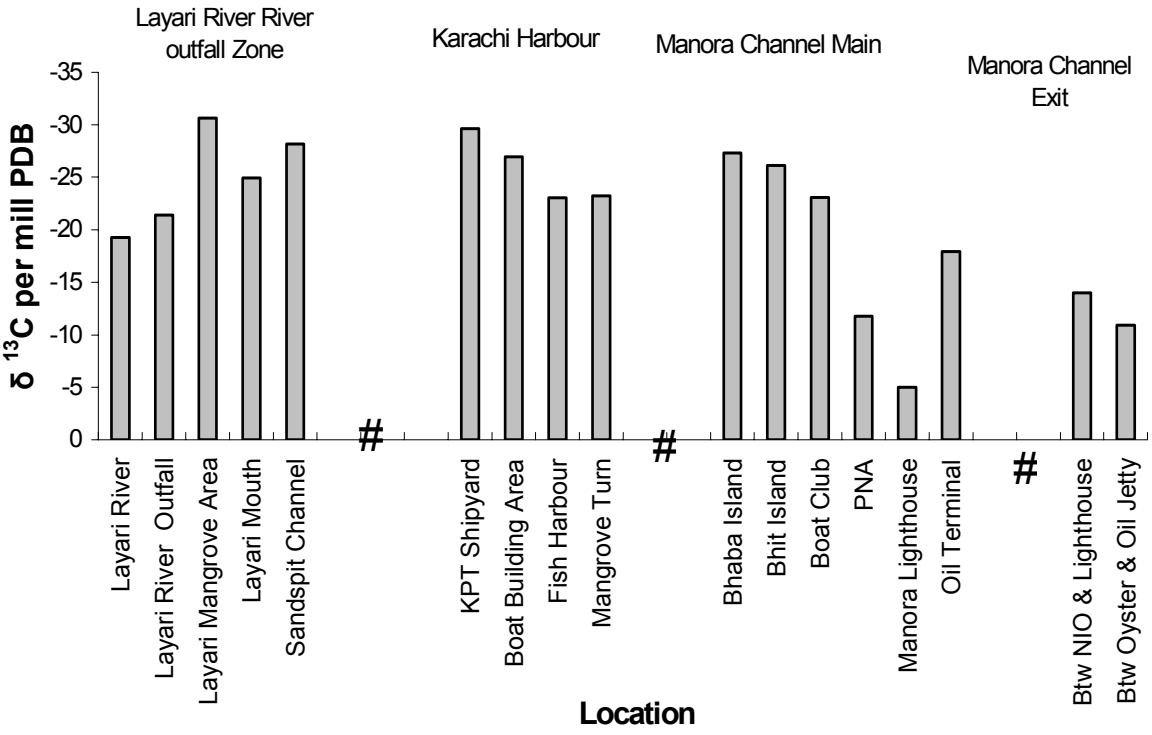

Figure 2. Stable Carbon Isotope (organic) in Manora channel sediment.

include delaying or raising the cost of maintenance dredging of navigational waterways due to the potential dangers of re-suspending particulate organic matter into the water column or the need to find disposal sites for the sediments. Organic pollution lead to a severe reduction in the diversity of bottom dwelling organisms that live in affected coastal regions and adverse effects can spread, via the food chain, to fish, birds, and mammals that feed on contaminated sea life. Those species that persist despite contamination may be subject to chronic ailments including diseases, deformities and reproductive maladies. The contamination of marine sediments becomes an important political issue when ports are dredged and contaminated dredged materials have to be dumped someplace, and it becomes a human health issue when fisheries are affected due to contaminated or diseased fish.

6. Conclusion

Good environmental quality is essential for sustaining coastal and marine ecosystems, commercial and recreational fisheries and economic growth in coastal communities. The health of coastal and marine ecosystems is affected by water and sediment quality . 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 study revealed that carbon isotope analyses of shallow marine sediment can serve a useful pollution indicator.

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