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STABLE ISOTOPIC TECHNIQUES TO ADDRESS MARINE POLLUTION: KARACHI COAST AS A CASE STUDY

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Seawater of the coastal regions near heavily industrialized and thickly populated urbanized centers normally receive large quantities of domestic, agricultural and industrial sewage. Ocean systems generally appear to be unlimited in their ability to dilute these human discharges and industrial wastes. This limit is now being exceeded in coastal waters in the vicinity of many large industrial and heavy populated coastal zones, causing threat to marine coastal resources of these areas. Considering the increasing threats of the unplanned inventory of untreated wastes into the marine coastal environment, the strength of isotope tools ($\delta^{13}C$) is used to understand the complex ecological systems in the marine coastal environment. This technique has been applied to study transport, behavior and fate of organic pollutants in marine coastal ecosystems of Karachi coast mainly as model studies. Carbon flow in heavily contaminated harbour channel (Manora Channel) , southeast and northwest coast have been investigated. The results indicate that shallow marine coastal waters tend to be depleted in $\delta^{13}C$ (TDIC) where polluted rivers through the coastal dwellings enter and get mixed with the seawater. Gradual increase in $\delta^{13}C$ (TDIC) are observed as the distance from pollution source is increased. Extremely depleted $\delta^{13}C_{org}$ was observed in sediment of Layari river outfall zone and Karachi fish harbor indicating input of domestic sewage through Layari river. Studies have proved that stable carbon isotope ratios of total dissolved inorganic carbon (TDIC) can be used as an effective tracer of sewage discharge and their transport in shallow marine environment.

Keyword: Stable isotope, Carbon, Nuclear techniques, Manora, Harbour

1. Introduction

Oceans are a big mixing vessels for the elements and compounds, either these are naturally formed or as a result of human activities. Its constituents are characterized by major components which do not appear to change their relative concentration with time, and by a much smaller fraction (less than 0.1% of the dissolved salts) in disequilibrium as a result of their participation in basic life processes, their introduction by humans as contaminants, or their geochemical reactivity [1]. The coastal areas are diverse and have productive habitats which are very vital for human settlements, development and local subsistence. More than half of the world's population lives within 60 km of the shoreline, and this could rise to three-quarters by the year 2020. Many of the world's poors are crowded in coastal areas [2].

The shallow coastal waters are an important part of the marine ecology, providing food and habitat to a large part of the commercial fish stock and a home for the growing marine culture industry. Threats to the ocean environment were first evident on its margins and therefore monitoring these waters should be a priority [3]. Pollutants due to urbanization, modernization, industrialization and various human activities are carried by rivers and ultimately dumped into the sea to pollute the vast water mass. Those pollutants which are not biodegradable cause irreversible damage to the marine ecosystem. The discharge of domestic and industrial effluents into the sea has resulted in a considerable increase in the concentration of some toxic elements, ionic species and man-made radionuclide in the sea water, sediments and marine organisms. This has in turn posed a significant threat to the marine life and occupational health of inhabitants of islands surrounded by polluted marine waters [4]. It is reported that a slight increase in the content of some contaminants can have adverse impacts not

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only on marine organisms but also on marine plants and animals and their ultimate transport through the food chain, may severely endanger human health. When chemical and metabolic processes scramble the information content of the molecules, isotopic compositions are often preserved. This realization has prompted increasing use of environmental stable isotopes for understanding complex ecological processes. Polluted water bodies carry unique isotope fingerprints which enable these inputs to be quantitatively distinguished within the mixing zones of estuaries, coastal and shelf waters.

2. Nuclear Techniques for the Study of Marine Pollution

There are variety of analytical techniques that can be used to address marine pollution related environmental issues [5]. Some commonly used marine pollution monitoring tools include: (i) Biological techniques (Coliform bacteria which used to determine type of bacteria involved in pollution generation through pollutant degradation or have health risks), (ii) Chemical techniques (BOD, COD, redox, turbidity, electrical conductivity, nutrients, pesticides and toxic/trace metal concentrations in the sea matrix, used to measure the origin, types, fate, behavior and analytical concentrations of inorganic and organic pollutants), Nuclear techniques (stable isotopes viz. ^{2}H, ^{18}O, ^{13}C, ^{15}N, and ^{34}S, used to measure origin, type, fate, behavior, travel path length, residence time of pollutants in the system etc.). The choice of these techniques depends upon the nature of the pollutants and the pollution problem in the marine environment, availability of techniques and their cost economics. In many cases, precise and accurate measurements and clues are necessary and essential component of a marine study.

Nuclear techniques, by far, represent a tool which can do certain jobs easier, quicker, better, reliable, precise and sometimes cheaper than the competitive conventional non-nuclear environmental methods. These techniques have strong potential for study of marine pollution problems such as determination of pollution inventories and pollutant transport in the marine environment. These isotopes are present naturally in the water molecule and its dissolved compounds, waste matter, biota and geological materials. Due to fractionation effects, their abundance varies in different sources [6].

The relative deviation in the isotopic abundance ratios of an environmental sample (water, gas, mineral matter, etc.) relative to a standard is conventionally referred to as δ value (or delta value) and is commonly measured using Mass Spectrometers (MS). Conventionally, for an MS analysis of isotopes, the element of isotopic interest in a representative sample is converted into a suitable gas form (*for example, CO_2 for ^{18}O, ^{13}C, isotope analysis, SO_2 for ^{34}S isotope analysis, N_2 for ^{15}N isotope analysis and H_2 for deuterium or ^{2}H isotope analysis*) using glass vacuum lines. The prepared gas is then subjected to a mass spectrometer for measurement of the isotope ratio R of the heavy and light isotopes in the injected gas molecules are measured. The δ value is determined with respect to an international standard reference material (SRM). If the absolute ratio of the heavy to the most abundant isotope (say $^{13}C/^{12}C$) in a sample material (say aqueous carbonate or marine shells) is R_S and the corresponding ratio in standard is R_{St}, then the relative deviation δ (delta) is expressed as:

$$\delta = \{(R_S - R_{St}) / R_{St}\} \times 1000 \qquad (i)$$

The 'δ' values are often expressed as per mill (‰) Particular reference standard are used for study of isotope contents of a material. For stable isotope analysis of carbon in the marine carbon pool (or any carbon pool), the standard is PDB (Pee-Dee Belemnite). The symbol $\delta^{13}C$ represents the normalized difference of $^{13}C/^{12}C$ ratios of a sample and a standard.

3. Karachi Coastal Pollution Investigation using Stable Isotope Techniques

Stable isotope of carbon ($\delta^{13}C$) is used to investigate Karachi Coastal water pollution due to Layari and Malir rivers, which mainly carry Karachi Metropolitan wastewater.

3.1 Sampling

For sampling, Karachi coast was broadly divided into three zones such as (i) Manora Channel (ii) Southeast coast and (iii) Northwest coast. Seawater from Manora Channel was sampled from several sites, including Layari river outfall zone, Fish Harbor, KPT Shipyard Butti, KPT Shipyard, Kaemari Boat Basin, Bhaba Island, Bhit Island, Boat Club, Pakistan Navel Academy (PNA) and Manora Light house (Figure 1). Sampling sites along Southeast coast include Marina Plaza, Casino, Naval Jetty, Marina club, Gizri area and Ibrahim Haideri fish habour whereas along Northwest coast sampling sites are Manora island seaside, PNS Himalaya, Kakka pir, Bulej , Power and Sunari point (Figures 1 and 2). The location of sampling points was determined with Garmin GPS-100 Personal Navigator™ (M/S Garmin, 11206 Thompson Avenue, Lenexa, KS 66219).

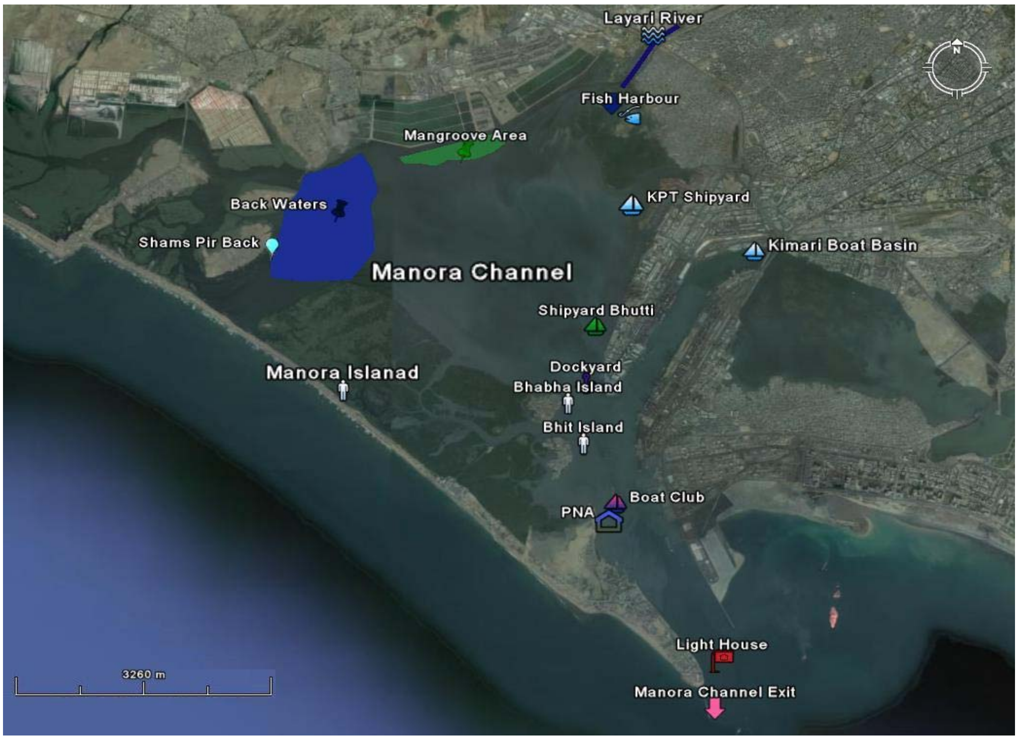

Figure 1. Location of sampling sites at Manora Channel.

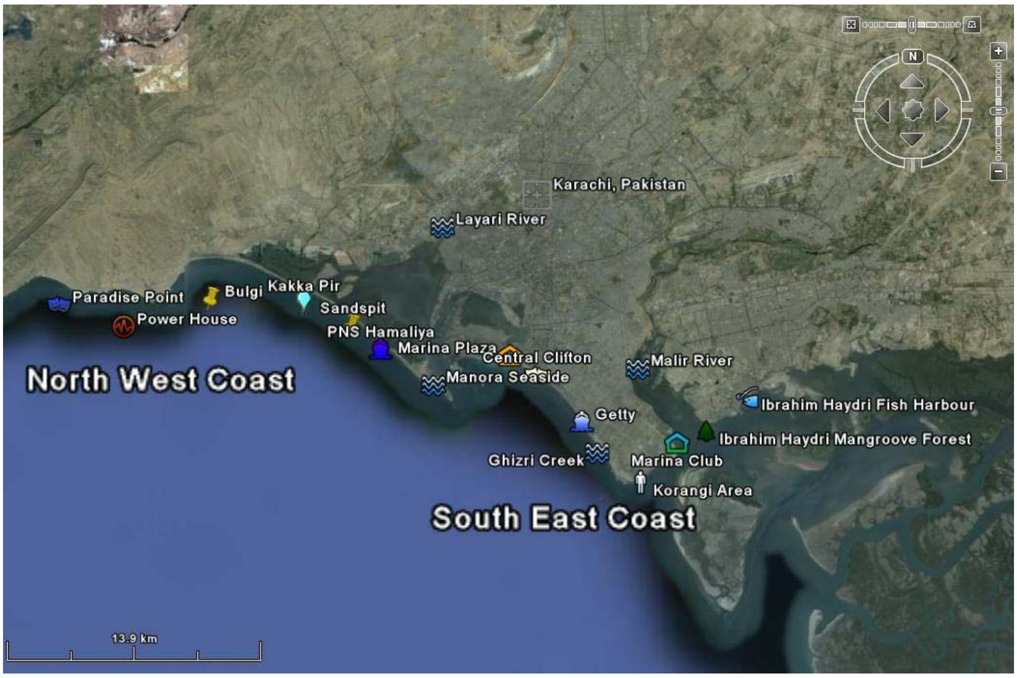

Figure 2. Location of sampling sites at southeast and northwest coast.

3.2. Sample Collection and Preservation

The period of field sampling was spanned over two years (April 2006 - September, 2008). This period was selected in order to cover overall variation in pollution transport pattern due to monsoon system. The sampling was started in April/May 2006 just in the beginning of summer monsoon. The second sampling phase was initiated in the winter monsoon (December 2007) when sea was relatively calm. The third sampling phase was completed in September, 2008 when the sea was almost quite. The sampling was accomplished using conventional mechanized boat. Sea water samples for isotope analysis were collected in accordance with standard procedures described elsewhere [7]. Sediments were sampled using Peterson Grab sampler during low tide period. This sampler was preferred because of its ability for sampling hard bottom material [8].

3.3. Stable Isotope Analysis

Stable carbon isotope analysis of total dissolved inorganic carbon ($\delta^{13}C_{TDIC}$) in water and organic and inorganic carbon in sediment samples was measured by extracting CO_2 gas using routine sample preparation methods [9]. All measurements were made on modified GD-150 Mass Spectrometer (Varian MAT, Germany). The results are expressed as $\delta^{13}C$ values relative to the international carbonate standard: PDB (Pee Dee Belemnite). The reproducibility of $\delta^{13}C_{TDIC}$ measurements was less than 0.05 ‰.

3.4 Results and Discussion

3.4.1 $\delta^{13}C_{(TDIC)}$ Analysis of Polluted Rivers and Coastal Water

The $\delta^{13}C_{(TDIC)}$ value for normal seawater is generally in the range of ± 1 per mill PDB [10] and $\delta^{13}C_{(TDIC)}$ values of waste drains are in the range of –16 to -10 per mill PDB [11]. Layari and Malir rivers water is depleted in $\delta^{13}C_{(TDIC)}$. The depleted values of $\delta^{13}C_{(TDIC)}$ in water of Layari river (-8.2 ‰ PDB) and Malir river (-8.8 ‰ PDB) due to the heavy influx of sewage.

The results in Figure 3 indicate that Manora Channel water is relatively less depleted in $\delta^{13}C_{TDIC}$ during high tide as compared to low tide conditions, which means that high tide environment retards the mixing of the municipal sewage into seawater. Hence, channel water is relatively more depleted in $\delta^{13}C_{TDIC}$ during low tide as it facilitates the diffusion of sewage pollution with seawater. The diffusion of sewage pollution appears to be gradually decreased as the distance of sampling site is increased from Layari river joining point with seawater and is shown by a progressive reduction in $\delta^{13}C_{TDIC}$ values (Figure 3). The $\delta^{13}C_{TDIC}$ values of seawater at PNA and Lighthouse are close to $\delta^{13}C_{TDIC}$ values of normal unpolluted seawater indicating less influx of sewage due to larger distance from the Layari river. Seasonal variation in $\delta^{13}C_{TDIC}$ values is attributed to strong currents and high flow of seawater in summer which hinders the mixing of sewage pollution as indicated by relatively less depleted values of $\delta^{13}C_{TDIC}$ as compared to weak currents and moderate seawater flow in winter.

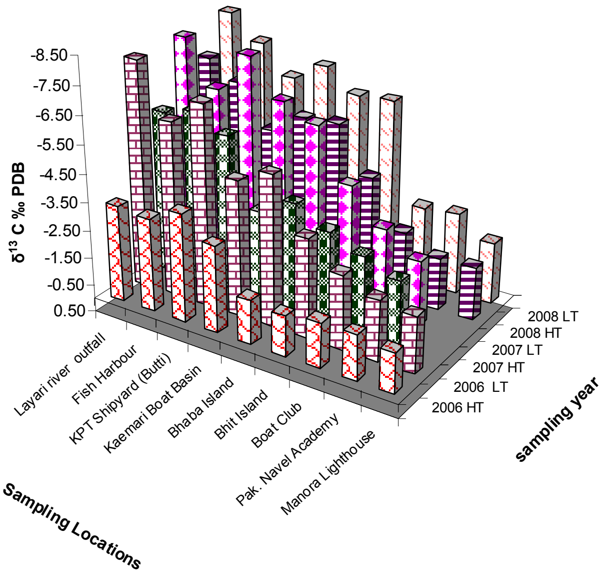

Figure 3. $\delta^{13}C_{(TDIC)}$ in coastal waters of Manora Channel.

Southeast coastal water is enriched in $\delta^{13}C_{(TDIC)}$ as compared to Manora Channel which indicates less influx of sewage pollution. However, considerable depleted values of $\delta^{13}C_{(TDIC)}$ are observed at Ghizri area where Malir river empties its pollution load (Figure 4). However, seawater of northwest coast exhibits fairly constant $\delta^{13}C_{TDIC}$ values (-0.2 to 0.46 ‰ PDB) which are close to normal seawater value and appears to be independent of tidal and seasonal effect (Figure 5). It indicates substantially low sewage pollution load as compared to Manora Channel and southeast coast.

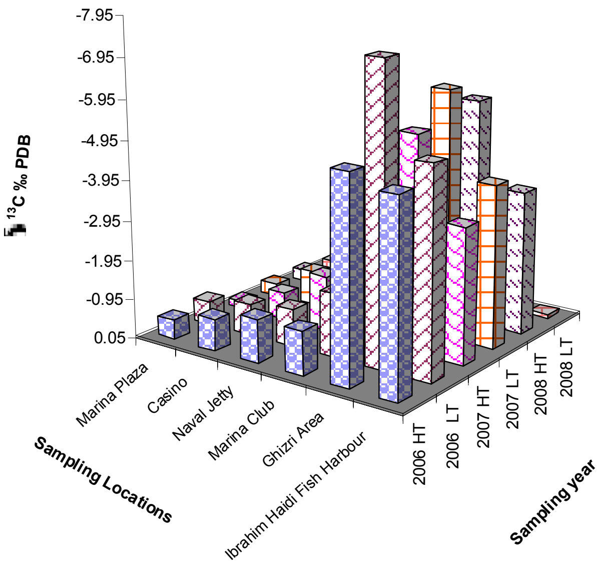

Figure 4. $\delta^{13}C_{(TDIC)}$ in coastal waters of southeast coast.

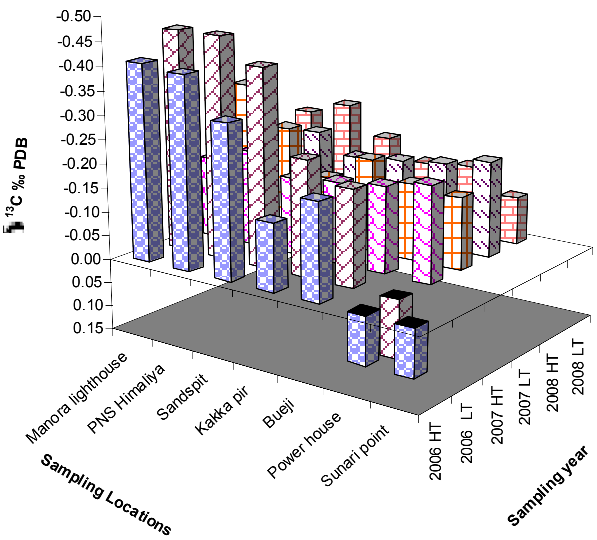

Figure 5. $\delta^{13}C_{(TDIC)}$ in coastal waters of northwest coast.

3.4.2. *Stable Carbon Isotope Composition of Sea Sediments*

$\delta^{13}C$ contents (inorganic and organic) of sediments from Karachi coast are shown in table 1. $\delta^{13}C_{inorg}$ values of Manora channel sediments varied from -2.7 to -0.6 ‰ PDB. Descolas-Gros and Fontugne, [12] also reported similar $\delta^{13}C_{inorg}$ values in the sediments originating from domestic wastewater. $\delta^{13}C_{org}$ contents were in the range of -26.5 to -7.0 ‰ PDB. The sediments from Layari river outfall zone and Karachi fish harbor appeared to be extremely depleted in $\delta^{13}C_{org}$ (-26.5 ‰), indicating domestic sewage as the main source.

Table 1. Stable carbon isotope composition of Karachi coastal sediments.

Sampling Zones	$\delta^{13}C$ (Inorg.) ‰ PDB	$\delta^{13}C$ (org.) ‰ PDB
Manora Channel		
Layari river outfall zone	-2.2	-26.5
Karachi Fish Harbor	-2.7	-26.5
KTP Shipyard (Butti)	-1.2	-15.4
Bhaba Island	-1.1	-18.6
Bhit Island	-0.6	-18.5
Boat Club	-0.7	-10.5
Pak. Navel Academy	-0.6	-11.7
Manora Lighthouse	-0.6	-7.0
Southeast Coast		
Marina Plaza	-0.7	-8.6
Casino	-0.7	-9.8
Naval Jetty	-0.7	-9.6
Marina club	-1 .0	-9.5
Ghizri Area	-1.9	-12.8
Ibrahim Haideri	-1.6	-14.9
Northwest Coast		
Manora Lighthouse (sea side)	-1.0	-9.1
PNS Himalaya	-0.7	-9.4
Sandspit	-0.3	-7.8
Kakkapir	-0.3	-8.1
Buleji	-0.3	-7.9
Power house	-0.3	-7.5

Sediments of Layari river outfall zone and Karachi fish harbor are predominantly clay which has much affinity for organic materials [13]. A gradual decrease in $\delta^{13}C$ contents (organic and inorganic) of sediments from Layari river outfall towards Manora Lighthouse is another important point to be noticed. It reflected that domestic waste matter reduces in the sediments of Manora channel with the increasing distance from joining point of Layari river into the sea at Layari river outfall zone to Manora channel exit. These results also support the physico-chemical characteristics and stable isotope analysis of seawater of Manora channel.

$\delta^{13}C_{org}$ contents of sediments of southeast coast were in the range of – 14.9 to -8.6 ‰ PDB. These values do not show any link with sewage material and indicate that sewage material carried through Malir River is diluted and dispersed by sea waves. However, low $\delta^{13}C_{org}$ values recorded in the sediments of Ghizri (-12.86 ‰ PDB) and Ibrahim Haideri (-14.9 ‰ PDB) might represent organic matter of dead phytoplankton [12]. $\delta^{13}C_{inorg}$ values of sediments pertaining to Northwest coast were in the range of -1.0 to -0.3 ‰ PDB and $\delta^{13}C_{org}$ ranged from -9.4 to -7.5 ‰ PDB indicating no domestic waste input in sediments.

4. Conclusion

Layari and Malir rivers water was observed to be depleted in $\delta^{13}C_{(TDIC)}$ which showed heavy influx of sewage into these rivers. In Manora Channel, where Layari river empties its pollution load, seawater was also depleted in $\delta^{13}C_{TDIC}$ during low tide environment showing a large scale domestic wastewater mixing with seawater. Southeast coastal water was found to be slightly enriched in $\delta^{13}C_{(TDIC)}$ that exhibited mixing of relatively small quantity of sewage with the seawater as compared to Manora channel. $\delta^{13}C_{(TDIC)}$ contents of northwest coastal water were close to the values for normal seawater. The studies demonstrated that stable carbon isotope ratio of seawater can be effectively used as pollution tracer.

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