SEAWATER POLLUTION STUDIES OF THE PAKISTAN COAST USING STABLE CARBON ISOTOPE TECHNIQUE

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ABSTRACT

Environmentally by stable carbon isotope ratios ($\delta^{13}C$ ‰ PDB) of total dissolved inorganic carbon (TDIC) have been used as a natural tracer of domestic and industrial pollution inventory in shallow seawater off the Pakistan Coast. Shallow seawater samples (sea depth range ~2-20 meters) were collected from five locations off the Baluchistan Coast (Jiwani, Gwadar, Pasni, Ormara, Sonmiani) and two locations off the Sindh Coast (Karachi and Indus Delta). Physiochemical parameters, such as pH, electrical conductivity, and Salinity, were measured in-situ. $\delta^{13}C$ values of TDIC were measured, using gas-source mass spectrometry. Significantly depleted $\delta^{13}C_{TDIC}$ values (as low as -7 per mill. PDB) coupled with measurable depletion in pH, electrical conductivity and salinity are observed in samples of seawater collected off the Indus Delta, Karachi coast, Gwadar coast and Sonmiani Bay. This is indicative of considerable inputs of pollution from industrial and/or domestic waste-drains into the marine environment off these coasts. The mangrove ecosystem is also found to strongly control the $\delta^{13}C_{TDIC}$ composition of seawater in the narrow channels of Jiawani Bay, Sonmiani Bay and in the backwaters of semi-closed Manora Channel.

INTRODUCTION

There is a serious lack of consciousness about marine pollution in Pakistan. Inadequate disposal of untreated industrial effluents and domestic sewage into shallow seawater off large coastal dwellings is a common practice. This has resulted not only in significant degradation of quality of sea-water but has also affected the biotic life, specifically along the coast of Karachi. Some sporadic surveys, involving use of classical hydro-geochemical and biological techniques, have been made in the past to estimate the pollution along the coast of Pakistan[1-4]. Environmental isotopes provide a complementary tool to deduce valuable information about the sources of pollution, as well as distribution and fate of pollutants in the hydrosphere, including the marine environment. Among these, the stable isotopes of carbon have a strong potential for determination of pollution-inventories from domestic and industrial sources (carbon flow) and pollutant-transport in the marine environment[7-9]. Stable carbon isotope ratios ($\delta^{13}C$ per mill PDB) of total dissolved inorganic carbon (TDIC) have been used as potential indicators of seawater-quality off the Karachi coast[8]. The stable carbon isotope ratios of marine environmental samples are of prime importance, as carbon makes up a dominant part of the marine ecosystem (living environments, marine geological matrix and the domestic and industrial waste matter). The $^{13}C/^{12}C$ ratios in various carbon reservoirs differ, due to fractionation-effects of certain biological, geological and chemical processes. Carbonate equilibria and photosynthetic conversion of inorganic carbon into organic carbon are major processes of carbon isotope fractionation in aquatic systems. Generally, organic matter is depleted of ^{13}C, with respect to inorganic carbon. Marine and land plants have different $\delta\ ^{13}C$ values. Potential pollutants, such as crude oil, effluents from petrochemical plants, in some instances, can be distinguished from natural marine dissolved organic carbon (DOC), particulate organic carbon (POC) and sedimentary organic carbon. Furthermore, CO_2 from effluents of domestic sewage has ^{13}C values much lower than the natural dissolved CO_2 in marine environment and ^{13}C potentially could be used as a pollution tracer. The general spectrum of $\delta\ ^{13}C$ in selective carbon reservoirs (or pools) in terrestrial and marine environment is shown in table - 1.

During November-December, 2000, shallow seawater samples were collected from seven selected locations along the coast of Pakistan i.e. the Baluchistan coast, and the Sindh Coast, for studies related to the IAEA/RCA/UNDP Marine Sub-project entitled: Management of Marine Coastal Environment and its Pollution (RAS/8/083). A component of this sub-project deals with determination of the levels, behaviour and the fate of pollutants in the marine coastal environment, using nuclear techniques. This paper documents the use of

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environmental stable carbon isotope technique to establish a pollution-scenario of shallow marine coastal environment of Pakistan.

supports the spawning and breeding grounds of commercially important shrimps as well as for a variety of other fishes. In the absence of an alternative resource, mangroves also serve the underprivileged inhabitants of coastal communities as a valuable source of timber, charcoal and fodder for domestic animals. The environmental pollution issues in the coastal zone of Pakistan have arisen mainly due to indiscriminate discharge of untreated effluents, domestic sewage and solid wastes, as well as agricultural runoff from coastal dwellings into the marine coastal environment. Increasing pollution along the Karachi coast has resulted in considerable thinning of the mangrove forests. The recent incidences of fish-kills off the Karachi coast and Gawadar Bay have been attributed to the growing pollution in shallow marine environment of these coasts[9].

Table - 1:
$\delta^{13}C$ Values for Various Reservoir/Pools

Carbon Pool	$\delta^{13}C$ ‰ PDB
Atmospheric CO_2	- 9 to - 6
Soil CO_2	- 30 to - 6
Groundwater DIC	- 20 to 0 (may be more up to +14)
Marine Dissolved Inorganic Carbon (DIC)	- 8 to + 2
Marine Particulate Organic Carbon (POC)	- 26 to -18
Marine Dissolved Organic Carbon (DOC)	- 30 to -18
Organics in Marine Sediments	- 38 to -17
Marine Limestone	- 5 to + 4 (may be more up to +7)
Marine Plants	- 16 to -4
Land Plants	- 28 to -16
Biogenic Methane	- 80 to - 40
Coal	- 27 to -22
Crude Oil	- 30 to -22
Pulp Mill Effluents	- 32 to -18
Domestic Sewage CO_2	- 12 to - 6
Domestic Sewage POC	- 20 to -16
Domestic Sewage DOC	- 26 to -22
Petrochemical and Natural Gas	- 30 to - 50 (or more depleted)

DESCRIPTION OF STUDY AREA

Pakistan has a coastline of 960 km, bordering the Arabian Sea. It extends from the border of India near Rann of Katch in the South-East to the border of Iran near Jiawani in the North-West (Figure - 1). The Exclusive Economic Zone (EEZ) is about 240,000 sq km. On the basis of its physiographical characteristics, the coastal area of Pakistan is divided into two distinct sections, namely, the Sindh Provincial coast and the Baluchistan Provincial coast (length: ~745 km). The Sindh Provincial Coast mainly includes the Indus River Delta-zone and the Karachi coast. With the exception of the Karachi metropolis (population over 12 millions and industrial base over 1000 large industrial units) along the Sindh coast, most parts of the coastal areas of Pakistan are sparsely inhabited. The entire coast of Baluchistan has small coastal towns and developing harbours, such as Jiawani, Gwadar, Pasni, Ormara and, Sonmiani, which have a total population of about one million. The coastal zone of Pakistan supports both living and non-living resources, which annually contribute towards the national economy. The mangrove ecosystems of the Indus deltaic region, Sonmiani Bay, and Jiawani are also of significant economic as well as scientific interest to Pakistan. The mangrove habitat

SAMPLING SITES AND FIELD METHODS

About 500 ml seawater samples (depth ~ 2 -20 meters) were collected in pre-cleaned and leak-tight plastic bottles. Samples were collected from seven principal coastal locations, namely: Jiawani, Gwadar, Pasni, Ormara, Sonmiani, Karachi and Indus Delta, along the coast of Pakistan during the period Nov.-Dec., 2000 for stable carbon isotope analysis ($\delta^{13}C$) of total dissolved inorganic carbon (TDIC). The samples were immediately spiked with 0.1M $HgCl_2$ solution to avoid additional input of inorganic carbon by

bio-mediated decomposition of organic matter in the samples. Samples were collected during the low-tide regime as, in this regime, the polluted river and sewage drains have adequate flow of water towards the sea. The samples were filtered through Whatman-42 and 0.45 micron nitrocellulose filter-paper in the nearby base-camp laboratory within 24 hours. The time for the occurrence of a low or high tide was deduced from the standard Tide Table Guide published by the Pakistan Navy. At some locations, waste drains/polluted rivers were also tapped during the last hour of low tide in the sea and at a suitable location in pre-outfall zone, so as to exclude the influence of high-tide intrusion of seawater in the polluted channel. Physiochemical parameters, such as pH, electrical conductivity and salinity, were measured in-situ.

LABORATORY METHODS

Stable carbon isotope analysis of total dissolved inorganic carbon (TDIC) in water-samples was determined by gas-source mass spectrometry and using routine sample-preparation methods[5,6]. Seawater sample (~250 ml) was reacted with 85% pure H_3PO_4 acid to liberate CO_2 gas from TDIC in a vacuum line. The moisture in the evolved CO_2 gas was condensed in a U-trap held at -80 ^oC, using freon-liquid nitrogen slush. Residual moisture in the evolved CO_2 gas was condensed in a subsequent U-trap, held at liquid nitrogen temperature (-196 ^oC). When the reaction was completed, the first U-trap was closed and the temperature of the second U-trap was raised to -80 ^oC with "freon-liquid nitrogen slush" to evaporate and expand the sample CO_2 in the vacuum-line for pressure measurements and to transfer it in a suitable vacuum-tight Pyrex glass ampoule for stable carbon isotope analysis on a modified GD-150 Mass Spectrometer. The stable carbon isotope results are expressed as δ *(delta)* ‰ *(per mil)* values relative to the international carbonate standard, namely, PDB *(Pee-Dee Belemnite):*

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

where R= $^{13}C/^{12}C$ ratio, S= unknown sample and St= known standard or reference material. The reproducibility of $\delta^{13}C$ measurements was better than 0.05 ‰ PDB for the working standard.

RESULTS AND DISCUSSION

Unpolluted seawaters have $\delta^{13}C_{TDIC}$ values closer to 0 ‰ PDB. Any deviation from this value will signify input of dissolved inorganic carbon from a secondary source. The coast of Baluchistan province is sparsely populated and there are no industrial activities up to now along this coast. However, untreated domestic sewage is drained into the sea from sizable dwellings (developing harbours) along this coast. Table - 2 presents a summary of the measured ranges of physiochemical parameters and $\delta^{13}C_{TDIC}$ contents for the marine coastal waters collected off the Baluchistan Coast. $\delta^{13}C_{TDIC}$ contents of clean seawater collected off the five coastal locations along Baluchistan coast range between +0.6 to -0.7 ‰ PDB. The positive values of $\delta^{13}C_{TDIC}$ are observed in shallow seawater collected off Jiawani Coast and Ormara Coast, whereas the negative values of $\delta^{13}C_{TDIC}$ are observed for Gwadar, Pasni and Sonmiani Bay. It is important to note that relatively clean surface seawater samples are collected from approximately 5 - 10 meter bathymetry line and their $\delta^{13}C_{TDIC}$ values are closer to typical seawater carbonate alkalinity. In contrast, the shallow seawater samples collected in the nearly inter-tidal zone (depth > 2 meters) of these coasts represent $\delta^{13}C_{TDIC}$ contents between -2.6 to -0.6 ‰ PDB. The shift in $\delta^{13}C_{TDIC}$ contents of clean seawater towards more negative values is indicative of input of ^{13}C depleted dissolved inorganic carbon, originated from domestic sewage drained into the sea by the adjacent dwellings along these coasts. It is important to note that relatively more depleted $\delta^{13}C_{TDIC}$ contents are observed in the mangrove ecosystem along Sonmiani Coast and Jiawani Coast. The values of $\delta^{13}C_{TDIC}$ tend to enrich in the direction of relatively clean seawater as we move out of the mangrove ecosystem. The higher depletions in $\delta^{13}C_{TDIC}$ values of seawater in Sonmiani Bay and along Jiwani Coast are thus attributed to the influx of carbon from the adjacent mangrove ecosystem ($\delta^{13}C_{mangrove\ leaves}$ ~ -26 ‰ PDB). This means that the ^{13}C depleted CO_2 is being produced by the decay of mangrove-leaf litter and is then incorporated into the TDIC pool of seawater as HCO_3^{-1}. Further, depletion in $^{13}C_{TDIC}$ contents of seawater are coupled with decrease in salinity and pH. The salinity is mainly decreased in zones adjacent to coastal dwellings.

The coast of Sindh province is heavily populated along the coastal city of Karachi and there are significant industrial activities along this coast. Seawater along Karachi coast thus receives large proportions of untreated domestic and industrial sewage, as well as

Table-2: Summary Of Physiochemical And Stable Carbon Isotope Analysis (C_{TDIC}) In Seawater And Polluted Drains Along Baluchistan Coast (Pakistan)

Coastal location in Baluchistan Province (n= total samples) [Lat/Long]	*Physiochemical parameters*			*Stable carbon isotope analysis*
	pH	***E.C. (mS)***	***Salinity (ppt)***	***$\delta^{13}C_{TDIC}$ (‰ PDB)***
Jiwani (n=7) *[N 25-02-61, E 67-44-47 to N25-02-82, E61-44-12]*	8.7 - 8.8	51.4 - 55.7	41 - 43	Clean Sea: +0.3 (n=1) Mangrove Zone: -0.4 to -1.9 (n=2) Populated Coast*: -1.4 to -0.6 (n=4)
Gwadar (n=9) *[N 25-06-23, E 62-23-53 to N 25-06-81, E62-19-85]*	8.1 - 9.2	52.5 - 57.1	40 - 47	Clean Sea: -0.1 (n=1) Polluted Drain: -4.7 (n=1) Populated Coast: -1.8 to -0.9 (n=7)
Pasni (n=5) *[N 25-5-65, E 23-28-71 to N 25-16-39, E63-28-71*	8.7 - 8.8	54.4 - 54.8	41- 45	Clean Sea: -0.5 (n=1) Populated Coast: -1.9 to -1.4 (n=4)
Ormara (n=5) *[N 25-13-03, E 64-38-25 to N 25-12-19, E64-40-34]*	7.9 - 8.2	55 - 56.4	38 - 40	Clean Sea: +0.6 (n=1) Populated Coast: -1.1 to -0.6 (n=4)
Sonmiani Bay (n=7) *[N 24-48-80, E 66-59-67 to N 25-26-29, E66-31-71]*	8.0 - 8.5	48.4 - 50.9	37 - 47	Clean Sea: -0.7 (n=1) Mangrove Zone: -2.2 to -3.7 (n=2) Populated Coast: -2.6 to -1.4 (n=4)

agricultural run-off, from adjacent dwellings and industrial zones. The Indus River has mostly dried in the delta zone due to tapping of Indus river-water in Tarbela Dam, Headworks on Indus River and due to very little rainfall in the area during past several years. However, the Indus delta Zone has small dwellings and creeks/mangrove ecosystems. Table-3 present a summary of the measured ranges of physiochemical parameters and $\delta^{13}C_{TDIC}$ contents for the marine coastal waters collected from selective sites off the Sindh coast (Pakistan). As expected, $\delta^{13}C_{TDIC}$ contents of seawater off Karachi coast and in the Indus delta zone are relatively more depleted, as compared to polluted zones along Baluchistan coast. Significantly depleted $\delta^{13}C_{TDIC}$ values (as low as -1.7 to -7.3 ‰ PDB) are observed in the Manora Channel/Karachi Harbour area and the Ghizri-Korangi Coastal area along Karachi coast. This is attributed to the large input of domestic waste and industrial waste from Layari River, Malir River and other small polluted drains into sea-environment. Seawaters collected off Korangi coast and Indus Delta along the Sindh Coast represent a decrease in pH by about 0.5 - 1 pH units. The decrease in pH along Korangi coast is attributed to input of mainly untreated industrial-waste waters and partly domestic sewage into the sea. The decrease in pH along Indus Delta is mainly due to influx of relatively low pH waters pertaining to Indus river and sewage from the nearby coastal dwellings/villages. The decrease in pH is also associated with decrease in the values of electrical conductivity and salinity. Further, the Indus delta seawaters are relatively less polluted, as compared to the seawaters off Karachi coast.

CONCLUSIONS:

In general, this study concludes that:

a. Stable carbon isotope contents of total dissolved inorganic carbon (TDIC) can be used as a potential indicator of pollution-inputs from domestic and industrial sources, as well as carbon flow into the

Table-3: Summary of physiochemical and stable carbon isotope analysis of (TDIC) in seawater and polluted drains along Sindh coast (Pakistan)

Coastal location in Sindh Province (n= total samples) *[Lat/Long]*	Physiochemical parameters			Stable carbon isotope analysis
	pH	E.C. (mS)	Salinity (ppt)	$\delta^{13}C_{TDIC}$ (‰ PDB)
Karachi Coast (n=31), [N 24- 47-53, E 66-59-77 to N 24-48-42, E67-17-18]				
Manora Channel (n=11)	8.2 - 8.5	43.7 - 50.8	28 - 36	Mangrove Zone: -5.1 to -7.3 (n=2) Polluted Drain: -3.7 to -6.0 (n=2) Populated Coast*: -6.8 to -1.7 (n=7)
Clifton -Marina Club Coast (n=7)	8.0 - 8.2	50.9 -55.6	37 - 41	Polluted Drain: -2.5 (n=1) Populated Coast: -3.1 to -0.2 (n=6)
Ghizri-Korangi Coast (n=8) **North-west Coast (n=7)**	7.3 - 7.9	51.4 - 55.3	39-41	Polluted Drain: -2.7 (n=1) Populated Coast: -6.6 to -3.0 (n=7)
	ND*	53.4 - 55.8	39 - 40	Clean Sea: +0.4 ** (n=1) Populated Coast: -5.3 to +0.3 (n=6)
Indus Delta (n=6) *[N 24-08-41, E 67-26-83 to N24-03-29, E67-41-46]*	7.3 - 8.3	46.6 - 56.5	32 - 45	Populated Coast: -2.3 to -1.4 (n=6)

ND = Not Determined
* *Seawater samples from shallow marine environment opposite coastal dwellings*
** *Seawater sample off Paradise Point, North West Coast of Karachi*

seawater from domestic and industrial sources as also from the mangrove ecosystems.

b. The shallow marine environment along the Baluchistan Coast is relatively much less polluted, as compared to the Sindh Coast

c. Ormara Coast is the least polluted marine site of the developed zone along Baluchistan coast.

d. The North-West Coast of Karachi is the least polluted marine site off Karachi city coast

e. The most depleted $\delta^{13}C_{TDIC}$ values of seawater in Sonmiani Bay and Jiawani Bay are due to the impact of mangrove ecosystem.

f. Extremely depleted $\delta^{13}C_{TDIC}$ values of shallow seawater off the Karachi Coast indicate that Manora Channel and Korangi Creek are the most polluted marine sites off the Pakistan coast. The North-west Coast and the Clifton coast are relatively less polluted coasts.

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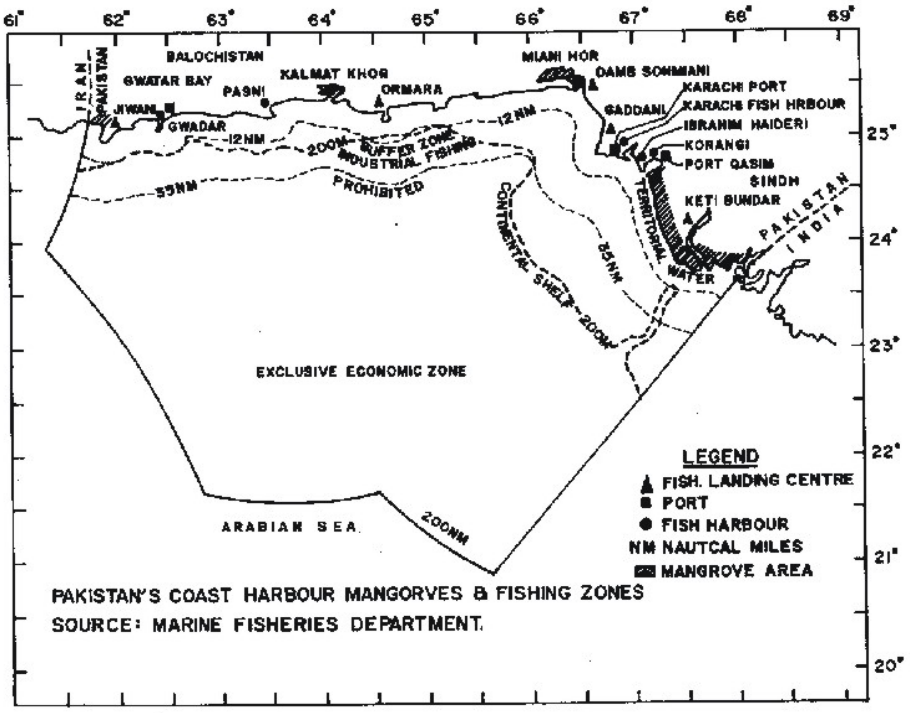

Figure – 1: Pakistan's Coast Harbour Mangorves & Fishing Zones