ISOTOPE HYDROCHEMICAL EVALUATION OF GROUNDWATER SALINITY IN COASTAL KARACHI, PAKISTAN

By

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Abstract:

The stable environmental isotopes such as δ^2H, $\delta^{18}O$, $\delta^{13}C$ and physico-chemical techniques are used for the investigation of saline water intrusion into portable groundwater in the coastal aquifer of Karachi Pakistan. Conjunctive use of hydrochemical and nuclear techniques is applied for origin of groundwater salinity in the potable shallow and deep groundwater in coastal aquifer of Karachi. Water samples from seawater, surface/groundwater were collected from various locations along polluted streams/rivers namely: Layari River and Malir River, Hub Dam, Hub River and local sea shallow seawater off Karachi coast during period of 2001 to 2003 from chemicals and stable isotope analysis. Physico-chemical parameters such as pH, Electrical conductivity (E.C.), Salinity were measured insitue. The hydro-chemical and stable isotope results indicate that the shallow/phreatic aquifers are recharged by a mixture of fresh waters of Indus River and Hub River as well as polluted Layari and Malir rivers and their feeding drains both under natural infiltration conditions and artificially induced infiltration conditions and to a much smaller extent from direct recharge of local precipitation. As for as deep groundwater is concerned, the confined aquifer hosts a mixture of rainwater from hinterlands and surrounding regions around coastal Karachi as well as sea trapped water/seawater through intrusion under natural infiltration conditions or under induced recharge conditions.

1. Introduction to the Problem

Coastal Karachi is by far, the most populous (~10 million in Habitants as per 1998 census) and the largest industrial (more than 1000 large industrial units) base of Pakistan with a coastline extending up to about 80 km. In Karachi freshwater resources are very few. The available shallow groundwater and deep groundwater is exploited for certain domestic and industrial area. Prolonged over-pumping of groundwater or other alterations of the natural equilibrium between recharge and discharge regimes of coastal aquifer system in Karachi can lead to an encroachment of the interface between seawater and freshwater, through intrusion and/or up-coning. Contamination by salty seawater can further elevate deterioration of groundwater quality in the coastal aquifer. A two to three percent mixing of coastal aquifer water with seawater makes freshwater unsuitable for human consumption. A five percent mixing makes it unusable for irrigation [1].

2. Description of Study Area

Hydrogeologically, the city of Karachi lies in the Hub River Basin and the Malir River Basin. The Malir River Basin is drained by the Malir River and the Layari River. The coastal aquifer of Karachi is, therefore, mainly recharged by seepage from Hub River, Hub Dam as well as the Malir and the Layari Rivers. The Hub River lies on the western frontier of Sindh and for some distance the boundary between Sindh and the Baluchistan provinces. It flows about 30 kms to the west of Karachi along the Karachi-Lasbela boundary. It falls into the Arabian Sea near Cape Monze, with a total drainage course length of 336 kms. Its principal tributaries are the Saruna, the Samotri and the Wira Hub. Hub River gradually widens and for some 80 kms from its mouth, is bordered by fine pastureland. Water is always found in pools, but the river is being utilized for irrigation and drinking purposes after building of the Hub Dam in the north-west of Karachi in the year 1980. The Hub Dam is 46 meters above the downstream riverbed. The dam has a gross

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storage of 1000 million cubic meters submerging about 8,000 ha of barren land. Its live storage is 920 million cubic meters with a life of ~75 years. The canal system is 32 kms of main canal, 35 kms of branch canal and 40 kms of minors. The main canal capacity is 370 cusecs. A canal of 200 cusecs capacity is designed to supply 89 MGD to the city of Karachi, 15 MGD to the city of Lasbela and 167 cusecs to irrigate 8400 ha of land in the Bela District. The Malir River Basin hosts the Malir River and the Layari River and lies in the coastal belt. The Malir River flows in the east of Karachi while the Layari River flows through the heart of Karachi city. In the up-stream region, these rivers have important streams that drain the hinterlands of Karachi. These rivers have been the source of fresh water supply for the Karachi metropolis for quite some time. However, both the watercourses are polluted with the passage of time due to input of vast quantities of untreated industrial and domestic wastes.

3. Water Supply Scenario for Coastal Karachi

Karachi has a complex water supply system that developed over a period of some more than 100 years. The shallow groundwater near the coastal belt is moderately saline. Today, the drinking water supply to most of the population in Karachi is managed through three schemes: (i) reserves in the nearby Hub Dam; (ii) exploitation of relatively adequate quality potable water in selective zones within the city by pumping wells and dug wells; (iii) pumping of piped water from the Indus River near Thatta City about 160 km away from Karachi. The Hub Dam reservoir capacity is insufficient to maintain long-term supplies of drinking water to the enormous population of Karachi. During the past 15 years, large number of pumping wells and open wells are installed into the Malir Basin to withdraw shallow and deep groundwater to meet requirements for the irrigation water supply (to raise vegetables, fruits, dairy and poultry) and drinking water supply for the ~10 million in Habitants of Karachi. Excessive pumping of groundwater and continuous depletion of water table is likely to result in seawater intrusion into the Malir Basin under natural seepage conditions and under artificially induced conditions of recharge of saline seawater in the coastal aquifer(s) of Karachi. It is feared that any further depletion of water table in coastal aquifer of Karachi will enhance seawater intrusion, thereby, affecting the drinking water quality of potable water in the coastal aquifer system. Ultimately, the whole aquifer water will be unfit for use not only for drinking purposes but also for domestic, industrial and irrigation purposes. It is, therefore, necessary to encourage groundwater recharge in the Malir River Basin on one hand and on the other hand define the existing water quality scenario of coastal aquifers of Karachi using modern & relatively precise techniques such as nuclear techniques so as to evaluate possibilities and impacts of seawater intrusion under heavy pumping of the Malir Basin.

4. Objectives

The growing concerns on deterioration of groundwater systems due to disposal of untreated domestic sewage and industrial effluents into surface water courses (mainly: Malir River, Layari River etc.) and its partial recharge under natural infiltration conditions and possibly under artificially induced infiltration conditions as well as saline sea water intrusion in coastal aquifers of Karachi are of great significance from hydrological, environmental and public health view point. Conjunctive use of hydro-chemical, biological and nuclear techniques can provide reliable information on dynamics of groundwater flow, origin and mechanism of groundwater salinity. Nuclear techniques such as environmental stable and radioactive isotope techniques can be used as reliable supplementary tools to conventional non-nuclear techniques to address these issues. As a first step, it was considered necessary to initiate primary studies to: (i) develop a general understanding about the isotopic, chemical and biological labeling of various recharge sources (rain, polluted streams/rivers, lakes, seawater) and the potable shallow and deep groundwater in coastal aquifer of Karachi, (ii) determine surface water and potable groundwater pollution characteristics, (iii) delineate spatial extent of saline groundwater, and (iv) to evaluate the possible role of seawater intrusion in the coastal belt of Karachi. It was decided to focus on evaluation of stable isotope characteristics of Oxygen (^{18}O) and Hydrogen (^{2}H) of the water molecule; stable isotopes of Carbon (^{13}C) in dissolved inorganic carbon, physiochemical and chemical characteristics (mainly parameters like E.C., salinity, pH and chemical activities of Chloride, Sulfate, bicarbonate) as well as Coliform bacterial characteristics of surface water sources (polluted rivers, lakes, precipitation, local seawater), potable shallow groundwater and deep groundwater sources (dug wells, hand-pumps, pumping wells which tap shallow and deep coastal aquifers of Karachi) and shallow sea water off Karachi Coast.

5. Present investigations

5.1. Field Sampling

Field sampling was performed in the jurisdiction of Karachi Metropolis during the period from November 2001 to December 2003. **Figure-1** shows the location of various sampling points. Surface water samples were collected from various locations along polluted streams/rivers namely: Layari River and Malir River, Hub Dam, Hub River and local sea (shallow seawater off Karachi coast). Shallow groundwater samples were collected from hand-pumps, dug wells and boreholes /mini pumping wells installed at depths upto 8 - 30 meters. Shallow mixed deep groundwater was collected from bore-holes/tube-wells installed at depths greater than 50 meters. Relatively deeper groundwater was collected from a few tube-wells installed at depths between 70-100 meters. All water samples were collected in leak-tight /lined cap plastic bottles or glass bottles. Sterile bottles were used for collection of water for Coliform bacterial analysis. Standard field sample preservation methods were used for subsequent chemical, biological and isotopic analysis in the laboratory **[2]**. In the field, all samples were stored under cool conditions ($<12\ ^0$ C). **Table-1** shows the area wise distribution of collected water samples.

The location of a seawater sampling point was monitored with the help of a Personal Navigator (Model Garmin™ GPS-100, M/S Garmin, 11206 Thompson Avenue, Lenexa, KS 66219). In the down stream zone, the rivers were tapped during the low tide period and at a point much beyond the influence of high tide so as to assure that river channels contained only the representative municipal waste waters and industrial effluents from polluted rivers.

Table-1: Inventory of collected water samples

Source of Water	**Locations**	Ist Sampling	2nd Sampling	3rd Sampling
Input Water Sources	Indus River (near Thatha)	2	1	
	Hub River	4	1	1
	Pollutant Rivers			
	Layari River	5	5	5
	Malir River	3	2	2
	Seawater (Karachi Coast:	6	6	6
	Precipitation (Rain)*	-------+		
Shallow Groundwater	Hand-pumps, Dug Wells. Shallow bore-holes / pumping wells	8	28	12
Deep Groundwater	Pumping wells/ Tube-wells	10	25	16

* = No rain during the sampling year + = Not determined / samples not collected

5.2. Field in-situ Analysis

Electrical conductivity, pH, turbidity and salinity were measured in-situe. Turbidity was measured with a portable turbidity meter (Model 6035, JENWAY). Electrical conductivity and temperature were measured with portable conductivity meter (Model HI 8633, M/S HANNA Instruments). Salinity was measured with a portable Salinometer (refractometer) obtained from the Center of Excellence in Marine Biology-Karachi University-Karachi.

5.3. Laboratory Analysis:

5.3.1. Coliform Bacterial Analysis: For the measurement of Total Coliform bacterial population and Faecal Coliform Bacterial population, accurately, 100 ml aliquots of a water sample were poured in two sterilized glass bottles. These were filtered separately to collect the Coliform bacteria onto 0.45 μ nitrocellulose membrane filter papers (Gelman Sciences, USA). Thereafter, the membrane filter papers were carefully put onto pads soaked in Membrane Lauryle Sulphate bacterial broth (ELE International Limited, U.K.) and placed in pre-labeled aluminum petri dishes. The dishes were placed in Paqualab^{TM} incubator (Paqualab Standard System 50, ELE International Limited, U.K.) for 16- 24 hours. One set of dishes was incubated at 44 ^{0}C for determination of the Faecal Coliform bacterial population, while the other set of dishes of same sample was incubated at 37^{o}C for determination of the Total Coliform bacterial population. Afterwards, the dishes were removed and the membrane filters were studied with a magnifying glass for presence of yellow spot colonies that confirm presence of Coliform bacteria in water samples **[3].**

5.3.2. Chemical Analysis of Water Samples: Major ion analysis of HCO_3^-, Cl^- and SO_4^{-2} on selective surface water and groundwater samples was carried out using UV-visible spectrometer (SO_4), ion selective electrode (Cl) and titrimetery (HCO_3).

5.3.3. Stable Isotope Analysis: Oxygen and Hydrogen isotope data are reported in the standard delta (δ) notation in parts per thousands (‰) to Vienna standard mean ocean water (VSMOW) [4]. The $\delta^{18}O$ values of the water samples were determined by the CO_2-H_2O equilibrated method [5] and measured using GD-150 Gas Source Ratio Mass Spectrometer. The δ D values of water samples were obtained by reduction to hydrogen over hot metallic Zinc [6] and measured using GD-150 Gas Source Ratio Mass Spectrometer. The reproducibility was better than ±0.1 ‰ (oxygen) and ±1‰ (Hydrogen). Stable Carbon Isotope Analysis of Total Dissolved Inorganic Carbon ($\delta^{13}C_{TDIC}$) in water samples was converted to CO_2 gas using routine sample preparation methods for mass spectrometric analysis by using 85% H_3PO_4 [7]. The measurement was 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 namely: PDB (Pee Dee Belemnite). The reproducibility of $\delta^{13}C_{TDIC}$ measurements was better the 0.05 ‰. Barium chloride was used for the precipitation of Sulphate into $BaSO_4$. The conversion of $BaSO_4$ to SO_2 for the measurement of $\delta^{34}S$ was carried out using V_2O_5 as catalyst. The $\delta^{34}S$ are expressed CDT [8].

6. Results and Discussion

It appears that five possible water sources are contributing to the groundwater storage in Karachi. The first possible source is the rainfall. As the city of Karachi suffers from deficit of precipitation (only rainfall), the contribution to shallow groundwater storage from rain is very little. However, rainfall in the hinterlands and other areas surrounding Karachi may significantly contribute to the confined groundwater flow system. The two freshwater sources are the Hub Lake/Hub Dam and the Indus River. Water from Hub Dam and the Indus River is piped to various residential zones in Karachi for drinking water and irrigation purposes. The spring water discharges into Malir River and Layari River and the municipal/industrial waste effluents added to these rivers are also contributing to groundwater storage as a fourth recharge source. Seawater intrusion along Karachi coast is the fifth possible source. Keeping in view this recharge scenario of surface water sources, we submit the following results / discussions w.r.t. our field and laboratory physico-chemical (pH, electrical conductivity, salinity and concentrations of major ion viz. HCO_3^{-1}, Cl^-, SO_4^{-2}), biological (Total and Fecal Coliform counts/100 ml) and isotopic (δ^2H, $\delta^{18}O$ $\delta^{13}C$, and $\delta^{34}S$) investigations of surface water and groundwater in Coastal Karachi-Pakistan. Tables 2-4 through present ranges of analyzed parameter for three year sampling.

6.1 Surface Water Sources

6.1.1 Local Precipitation (Rain)

During the sampling period, no rainfall events occurred in coastal Karachi. Therefore, it was not possible for the sampling team to collect and analyze local rain for chemical and isotopic information. However, stable isotope data on precipitation for the period from 1961 to 1975 is available from the IAEA Precipitation Network for the Karachi Station (IAEA Precipitation Network Code: 41780000, Lat. 24.90N Long. 67.13E, Alt. 23 meters above mean sea level) [9]. The following stable isotope indices of precipitation in Karachi were, therefore, used for interpretation purposes:

Long Term Weighted Means:

$\delta^{18}O$ (water): - 3.93 ± 1.94 ‰ V-SMOW

$\delta^{2}H$ (water): - 23.5 ± 18.1 ‰ V-SMOW

Long Term Monthly Correlation between $\delta^{18}O$ and $\delta^{2}H$ (LSF):

$$\delta^{2}H = [7.56\ \delta^{18}O \pm 0.34] + [3.41 \pm 1.50]$$

(r = 0.965)

6.1.2 Indus River

Physico-chemical, bacteriological and environmental stable isotope analysis was performed on water sample collected from the Indus River near Thatta city during three sampling (2001 to 2003). The physico-chemical parameters indicate that there is no significant changes in these values are observed during three years of sampling from 2001 to 2003. The SO_4^{-2} concentrations in the river water are ranges from 13-86 ppm. There is no change in the concentration of chloride contents during the sampling periods of 2002 and 2003. The stable isotope indices of total dissolved inorganic carbon (TDIC) in water, and of oxygen and hydrogen in water molecule, and stable sulfur isotope of sulfate are as following:

$\delta^{13}C$ (TDIC):	-1.66 to + 1.7 ‰ PDB	(n=3)
$\delta^{18}O$ (water):	-8.2 to - 5.9 ‰ V-SMOW	(n=3)
$\delta^{2}H$ (water):	- 62.8 to - 48.12 ‰ V-SMOW	(n=3)
$\delta^{34}S_{SO4}$:	6.28 ‰ CDT	(n=1)

6.1.3 Hub Dam

The water storage in the Hub Lake was very little because the Hub River was dry due to drought conditions in and around the study area over the past several years. Thus, most of the Hub Lake had patches of stagnant water. Hub Dam water was collected during sampling periods of 2001 and 2002. Except in Coliform bacterial population, different patches of water in the lake showed similar values of mildly alkaline pH (~8.2-8.8), E.C (~1.1 to 1.5 mS/cm). The electrical conductivity values were three times higher than the Indus river water supply. Significant population of Total Coliform bacteria and fecal Coliform populations are observed during first and second sampling periods. This indicates that sewage/domestic waste is being continuously added into the dam waters. This is well indicated by the following enriched values of ^{18}O and ^{2}H contents of the lake water:

$\delta^{18}O$ (Hub Lake water):	+ 1.7 to + 2.9 ‰ V-SMOW	(n=5)
$\delta^{2}H$ (Hub Lake water):	+0.9 to +11.8 ‰ V-SMOW	(n=5)
$\delta^{13}C$ (Hub Lake water):	+1.0 to +6.3 ‰ PDB	(n=5)

The stable carbon isotope index ($\delta^{13}C_{TDIC}$) of total dissolved inorganic carbon in lake water varies in the range of +1‰ PDB to + 6.3 ‰ PDB in different patches of stagnant lake water. This is indicative of different sources of dissolved inorganic carbon in the lake (TDIC) into other carbon containing compounds over the drought regime.

6.1.4 Polluted Rivers

Layari River: The Layari River was monitored at locations along its flow from North Karachi (upstream region) to Sher-Shah Bridge (downstream region) near Keamari/Sea. The range of variation in stable isotope content of total dissolved inorganic carbon (TDIC) and of oxygen and hydrogen in Layari River water are as following:

$\delta^{18}O$ (Layari River Water):	-5.4 to -1.6 ‰ V-SMOW	(n=15)
$\delta^{2}H$ (Layari River Water):	-45.0 to -19.0 ‰ V-SMOW	(n=15)
$\delta^{13}C$ (TDIC-Layari River Water):	-9.6 to -0.2 ‰ PDB	(n=15)
$\delta^{34}S_{SO4}$:	7.2 to 8.9 ‰ CDT	(n=5)

Total Coliform and Fecal Coliform bacterial population in the Layari River water increased along the flow. The Total Coliform population ranges between 560 to $2.65x10^4$ per 100 ml water whereas, the Fecal Coliform population ranges between 540-$4.79x10^4$ per 100 ml water. Fecal Coliform population is quite dominant and of immense concern from health view point. High concentrations of Cl^- (233-3296 ppm) and SO_4^{-2} (33-525 ppm) coupled with mildly alkaline pH values are found in the upstream regions of the river. However, these values decrease significantly along the flow downstream whereby, the pH values remain slightly above neutral values. This indicates that the source of water in the upstream regions of Layari River is quite different than the downstream regions. The $\delta^{13}C_{TDIC}$ and $\delta^{18}O$ (water) values are also quite enriched at starting Point of Layari River as compared to local shallow groundwater and are in fact relatively closer to the sea values. Downstream, as the Layari River receives sewage water of the city, which is a mixture of the Indus River water, and the local shallow groundwater supplied to the city for domestic use, the values of $\delta^{18}O$ are consistently around -5 ‰ V-SMOW. It is thus, speculated that the water in the extreme up-stream region of Layari River is a mixture of deep groundwater which is partly trapped seawater (or geothermal water as there are geothermal springs nearby) and the local shallow groundwater.

Malir River: The Malir River was monitored at two - three locations along its flow from Karachi East to the Sea before Ghizri Creek during three sampling phase. The range of variation in stable isotope content of total dissolved inorganic carbon (TDIC) in water and of oxygen and hydrogen in Malir River water are as following:

$\delta^{18}O$ (Malir River Water):	-4.9 to +1.0 ‰ V-SMOW	(n=8)
$\delta^{2}H$ (Malir River Water):	-44.7 to –6.0 ‰ V-SMOW	(n=8)
$\delta^{13}C$ (TDIC - Malir River Water):	-8.7 to -1.4 ‰ PDB	(n=2)
$\delta^{34}S_{SO4}$	11.6 to 14.2 ‰ CDT	(n=2)

Lowest values of EC and Salinity were observed at the origin of the River behind Shah Faisal Colony. In this zone, the River receives minor spring water, minor domestic wastewater from small isolated dwellings and seepage from agricultural fields/vegetable farms that use the low E.C Indus River water supply for irrigation. Turbidity of the river increases along flow as it receives more and more water of industrial origin (mainly tannery wastes). Total Coliform and Fecal Coliform bacterial population in the river water increased along the flow. The Total Coliform population ranges between $4.5x10^3$ to $5.9x10^3$ per 100 ml water whereas, the Fecal Coliform population ranges between $1.9x10^3$ to $2.1x10^3$ per 100 ml water. This shows that the Fecal Coliform population which are indicators of sewage inputs, is quite dominant and of immense concern from health view point. The pH of the river water increases by one unit as it receives domestic and industrial alkaline effluents. High concentrations of Cl^- (2024 ppm) and SO_4^{-2} (271 ppm) are found in the downstream region of the river. This is perhaps due to the effect of sea tides in the Qayyum Abad area near Ghizri Creek.

6.1.5 Karachi Sea:

The pH values of ~8.5 for open seawater off Karachi Coast generally conform to those for normal ocean waters. However, pH values decrease to levels of ~7.7 near the Ghizri Creek and the Korangi Creek which receive significant quantities of industrial acidic wastewaters. Similarly, the pH values of seawater increase to ~8.5 in the backwaters of Manora Channel. Electrical

Conductivity values for Karachi seawater range between 49.3 mS/cm to 53.7 mS/cm while the salinity values are ~ 39 ppt. The electrical conductivity values higher than 53 mS/cm correspond to relatively non-polluted open seawaters on northwest and southeast sides of Karachi coast. The lowest E.C. values of 49.3 mS/cm and salinity value of 32 ppt correspond to mixing of mainly domestic and partly industrial wastewater from Layari River in Manora Channel backwaters. Turbidity values of open seawater are quite higher than the on-shore surface water sources (polluted Layari and Malir Rivers, Indus River and the Hub Lake). This is attributed to much higher contents of particulate matter in seawater as compared to on-shore surface water sources. The lowest values of turbidity are observed along Clifton coast, as this coast is relatively free of pollution along southeast side of Karachi coast. Coliform bacterial population is lower along non-polluted Clifton coast and the northwest coast. However, significantly higher Coliform counts are observed along polluted coastal spots along Karachi coast. Highest Coliform counts are observed along Ibrahim Haideri Fish Harbour zone along southeast coast of Karachi and the Manora Channel backwaters. Cl^- contents of seawater off Karachi coast are in the range of 21,578 to 25,230 ppm while the SO_4^{-2} concentrations are in the range of 2076 to 2323 ppm. The stable carbon isotope contents ($\delta^{13}C_{TDIC}$) of total dissolved inorganic carbon (TDIC) vary in the range of -3.9 ‰ PDB to + 0.8 ‰ PDB in different zones off Karachi coast. This is indicative of different levels and sources of dissolved inorganic carbon in seawater due to input of domestic and industrial wastewater into the sea from key industrial trading estates (LITE, KITE, SITE etc.) via polluted drains. The highest $\delta^{13}C_{TDIC}$ value of + 0.8 ‰ PDB corresponds to relatively non-polluted seawater along northwest coast of Karachi. The lowest $\delta^{13}C_{TDIC}$ value of -3.9 ‰ PDB corresponds to highly polluted seawater in Korangi Creek which receives industrial and domestic waste drains from Korangi Industrial Trading Estate (KITE). The high tide (HT) stable isotope content of oxygen and hydrogen in relatively non-polluted seawater along Karachi coast falls in the following range:

$\delta^{18}O$ (seawater)$_{HT}$:	+ 0.27 to + 1.1	‰ V-SMOW	(n=15)
$\delta^{2}H$ (seawater)$_{HT}$:	- 0.7 to + 8.6	‰ V-SMOW	(n=15)
$\delta^{13}C$ (TDIC - seawater):	- 3.9 to +0.8	‰ PDB	(n=15)

The low tide (LT) stable isotope content of oxygen in relatively polluted seawater along Karachi coast falls in the following range:

$\delta^{18}O$ (seawater)$_{LT}$:	- 1.3 to + 0.1	‰ V-SMOW	(n =15)

6.2. Potable Groundwater in Coastal Aquifer

Shallow groundwater samples were obtained from hand pumps (n=1), dug wells (n=1) and shallow bores with centrifugal pumps (n=8) installed at depths less than 50 meters (mainly between 8-50 meters); and (b) relatively deep groundwater obtained from pumping wells (cased wells/Tube-wells) installed at depths greater than 50 meters in the coastal aquifer of Karachi. These cased wells also tap various proportions of shallow groundwater in addition to deep groundwater. Tables 2-4 present the ranges of physico-chemical, bacteriological and stable isotope data of shallow and deep groundwater of three sampling (2001-2003). The following section presents discussion on these data elements.

6.2.1. Shallow Groundwater

Physico-chemical data of shallow groundwater (depth less than 50 meters) shows that the shallow wells located in the vicinity of coast and in the proximity of polluted rivers have relatively higher values of electrical conductivity, salinity and population of Coliform bacteria. Selective borehole/well samples in the vicinity of Layari River and Malir River have extremely high values of Total Coliform and Fecal Coliform bacteria. In general, the bacteriological quality of shallow groundwater is quite poor and renders the water unfit for drinking purposes without prior treatment. The shallow groundwater is moderately saline representing electrical conductivity values. However, some located near coastal belt have very high Electrical conductivity values (0.4 to 21.4 mS/cm). The pH of shallow groundwater varies from mildly acidic (~6.3) to mildly alkaline values (~8.3). Turbidity of shallow groundwater varies between 3.6 NTU to 142 NTU.

The concentration of HCO_3^- (164 - 630 ppm, n=48), Cl^- (56- 9031 ppm, n=48) and SO_4^{-2} (25-968 ppm, n=48) in general except for few samples is very reasonable.

The range of variation in stable isotope content of total dissolved inorganic carbon (TDIC) and oxygen and hydrogen in Layari River water is as following:

$\delta^{18}O$ (Shallow Groundwater):	- 7.2 to -3.0 ‰ V-SMOW	(n=48)
$\delta^{2}H$ (Shallow Groundwater):	- 54.0 to -27.0 ‰ V-SMOW	(n=48)
$\delta^{13}C$(TDIC - Shallow Groundwater):	-16.1 to -1.7 ‰ PDB	(n=48)
$\delta^{34}S_{SO4}$ of water:	2.7 to 8.7 ‰ CDT	(n=48)

The mean stable isotope content of ^{18}O and ^{2}H in shallow groundwater is as following:

Mean $\delta^{18}O$ (Shallow Groundwater):	-5.68 ± 1.84 ‰ V-SMOW	(n=48)
Mean $\delta^{2}H$ (Shallow Groundwater):	-46.5 ± 6.2 ‰ V-SMOW	(n=48)
Mean $\delta^{13}C$ (TDIC-Shallow Groundwater):	-8.13 ± 3.1 ‰ PDB	(n=48)

The correlation between $\delta^{18}O$ and $\delta^{2}H$ (LSF) for shallow groundwater is as following:

$$\delta^{2}H = 6.4\,\delta^{18}O - 10.2 \qquad (r = 0.61,\ n=48)$$

The stable isotope results indicate that the shallow /phreatic aquifers are recharged by a mixture of fresh waters of Indus River and Hub River (draining spring water and flooded rainwater) as well as polluted Layari and Malir rivers and their feeding drains (both under natural infiltration conditions and artificially induced infiltration conditions) and to a much smaller extent from direct recharge of local precipitation.

6.2.2 Deep Groundwater

In general, deep groundwater is mostly saline and has high electrical conductivity and salinity as compared to shallow groundwater. The sampled deep groundwater from pumping wells is in fact a mixture of various proportions of shallow groundwater from freshwater phreatic/unconfined aquifer and actual deep groundwater from the confined aquifer. In the absence of well logs of sampled tube-wells/pumping wells, it is not possible to estimate the proportions of inputs of shallow groundwater in the discharge of these wells. Based on hydro-chemical data, it is assumed that the shallow mixed deep groundwater discharged by large scale pumping wells mainly represents the deep groundwater from confined aquifer. The more representative deep groundwater wells are those that have relatively higher values of electrical conductivity (range: 1.9-32.5 mS/cm), salinity (range: 1.0-7.4 ppt) as well as concentrations of Cl^- (range: 170-12766 ppm) and SO_4^{-2} (range: 36-2413 ppm). The deep wells located close to the coast/shoreline also have relatively higher values of electrical conductivity, salinity, Cl^- and SO_4^{-2}. High counts of Total Coliform and Fecal Coliform bacteria was found in relatively less deep shallow wells installed in the Layari River belt. High counts of Total Coliform and Fecal Coliform bacteria was also found in relatively less deep shallow wells installed in poorly drained and poorly managed sanitary conditions.

The range of variation in stable isotope content of total dissolved inorganic carbon (TDIC) and oxygen and hydrogen in shallow mixed deep groundwater is as following:

$\delta^{18}O$ (Deep Groundwater):	-7.22 to -3.56 ‰ V-SMOW	(n=51)
$\delta^{2}H$ (Deep Groundwater):	-72.59 to - 26.7 ‰ V-SMOW	(n=51)
$\delta^{13}C$(TDIC - Deep Groundwater):	-13.2 to -0.3 ‰ PDB	(n=51)
$\delta^{34}S_{SO4}$ Deep Groundwater:	-12.04 to +17.9 ‰ CDT	(n=51)

The mean stable isotope content of ^{18}O and ^{2}H in shallow mixed deep groundwater is as following:

Mean $\delta^{18}O$ (Deep Groundwater):	-5.6 ± 1.3 ‰ V-SMOW	(n=51)

Mean δ^2H (Deep Groundwater): -43.9 ± 2.4 ‰ V-SMOW (n=51)
Mean $\delta^{13}C$(TDIC- Deep Groundwater): -7.9 ± 3.4 ‰ PDB (n=51)

The correlation between $\delta^{18}O$ and δ^2H (LSF) for shallow mixed deep groundwater is as following**:**

$$\delta^2H = 9.32\,\delta^{18}O + 7.0 \qquad (r = 0.95,\ n=51)$$

The hydro-chemical and stable isotope results indicates that the confined aquifer hosts a mixture of rainwater from hinterlands and surrounding regions around coastal Karachi as well as sea trapped water/seawater through intrusion under natural infiltration conditions or under induced recharge conditions.

6.3. Groundwater Recharge Characteristics/ Sea water Intrusion

Presently, coastal Karachi is known to have five sources of recharge to its groundwater reserves. These are: (i) rainfall, (ii) Indus River water supply, (iii) Hub-River & Hub Lake water supply; (iv) polluted Layari and Malir rivers/contributory channels draining mixtures of domestic, industrial and agricultural wastewater composed of pre-said three sources; and (v) seawater. The possibilities of major contribution to groundwater recharge of shallow/phreatic aquifer directly by local rainfall seems very small due to very poor frequency of rainfall events and rainfall intensities in the Karachi and high evaporation rates. The long term (15 years annual record) mean monthly average precipitation for Karachi is between 0-15 mm during the months of January to June, 23 - 91 mm during the months of July to September and 0-7 mm during the months of October to December **[3]**. The remaining four sources can play a significant role in recharge of the shallow aquifer system and deep groundwater system (confined aquifer) in coastal Karachi.

In order to postulate the origin of shallow and deep groundwater and related salinity in the shallow aquifer system and the confined deep aquifer system, the stable isotope composition of oxygen and hydrogen and hydro-chemical data of groundwater samples collected in present investigation is statistically evaluated.

Figure 2 shows the $\delta^{18}O$ versus δ^2H plot of groundwater in coastal Karachi vis-à-vis isotopic indices of local rainwater, Indus River water and local seawater. The large term mean stable isotope composition of ^{18}O and ^2H in precipitation falls on the Local Meteoric Water Line (LMWL), while the surface water samples (Hub Lake water and the river water, local seawater) and the groundwater samples fall below the local meteoric water line. Further, the large shift in $\delta^{18}O$ values of shallow and less deep groundwater towards right of Local Meteoric Water Line (LMWL) must be result of various possible process such as recharge of local precipitation, Indus River water and Hub River water used for domestic and agricultural irrigation purposes, followed by evaporation prior to recharge and recharge of mixed waters from polluted rivers.

The representative deep groundwater samples fall relatively closer to the LMWL in the vicinity of long term mean of precipitation in Karachi. There is a distinctly large spread of data for shallow groundwater samples and representative deep groundwater samples, thereby indicating distinct sources of recharge to the shallow aquifer system and the deep confined aquifer system. The shallow groundwater samples cluster around a mean $\delta^{18}O$ values of -5.6± 1.8‰ V-SMOW and clearly indicate strong effect of mixing of local precipitation recharge ($\delta^{18}O$ = -3.9 ±1.94 ‰ V-SMOW) with water from the Indus River ($\delta^{18}O$ = -8.2 ‰ V-SMOW).

Keeping in view the mean stable isotope indices of oxygen in local rainwater ($\delta^{18}O$ = -3.93±1.94 ‰ V-SMOW) and local seawater ($\delta^{18}O$: +0.1 to +1.1 ‰V-SMOW) as a major recharge source, shallow groundwater, deep groundwater, it may be realized that a strong impact of seawater intrusion in coastal aquifer system will shift the ^{18}O isotopic composition of both the shallow groundwater and deep groundwater towards the seawater $\delta^{18}O$ index. Nevertheless, $\delta^{18}O$ versus δ^2H plot of groundwater in coastal Karachi shows that the shallow groundwater trends in the direction of stable isotope index of ^{18}O and ^{2}H in Indus River water. It is therefore, speculated that under the present water supply practices and drought conditions, the stable isotope index of ^{18}O and ^{2}H in shallow and less deep groundwater will ultimately shift from local precipitation index to the direction of isotopic composition of the Indus River.

Unpolluted seawater off Karachi coast is characterized by a $\delta^{18}O$ value of ~ +1 ‰ V-SMOW and a chloride content of ~23000 ppm. Both the Layari River and Malir River waters as well as the Indus River water and the Hub Lake water have extremely very low aqueous contents of chloride and sulfate ions as compared to seawater. The average mean value of $\delta^{18}O$ in polluted river waters is ~5 ‰ V-SMOW and in shallow groundwater is -5.9 ‰ V-SMOW. Therefore, those pumping wells that are located near the coastline/shore line (where seawater intrusion could be expected) and have high chloride and sulfate values should represent seawater intrusion and relatively enriched ^{18}O values. However, for pumping wells located comparatively far away from the coast and representing high salinity (chloride & sulfate concentrations), the contribution of saline water may be derived from upward diffusion from the freshwater- seawater interface possibly as a result of local fluctuation of water table due to pumping. In present investigations, shallow mixed deep pumping wells installed near the coast have significantly high values of chloride (in both wells) and sulfate but have $\delta^{18}O$ values closer to polluted river water and shallow groundwater. This suggests that these coastal pumping wells are withdrawing significant quantities of water from shallow aquifer that also hosts recharge of seawater gushed into the coastal zone during summer monsoon period. However, possibilities of direct seawater intrusion in these wells under prolonged pumping conditions is yet to be verified. Noteworthy are the pumping wells with significantly high chloride content and relatively lower sulfate content. It is speculated that the lower sulfate contents are due to biological reduction of sulfate. Sulfur Isotopic analysis ($\delta^{34}S$) of aqueous sulfate indicates that the well situated close to the coast host the recharge of seawater. These well wells have values of $\delta^{34}S$ close to sea water.

The relatively deeper groundwaters representing confined aquifer have enriched $\delta^{18}O$ and excessively high values of aqueous chloride and sulfate. Some deep groundwater samples have $\delta^{13}C$ (TDIC) value very close to the $\delta^{13}C$ (TDIC) value for seawater. Some deep wells have depleted $\delta^{13}C$ (TDIC) values up to -13.2 ‰ PDB. Similar depleted $\delta^{13}C$ values have been reported for deep saline groundwater tapped from confined aquifer in the coastal zone of Orissa- India **[10]**. It is speculated that the groundwater tapped by these wells mainly represents a mixture of recharge from rainfall in the hinterlands, floodwater and spring water drained by the Malir River Basin and the Hub River Basin around coastal Karachi as well as seawater. For some wells located in Clifton areas, we speculate direct seawater intrusion by excessive pumping. However, incase of pumping wells with excessively high values of chloride and sulfate in deep groundwater away from the coast suggest possibilities of trapped seawater. To verify possibilities of seawater intrusion in shallow groundwater and mixed deep groundwater and/or existence of trapped seawater in deep groundwater, the concentrations of SO_4^{-2} (in milligrams per liter, log scale) are plotted against SO_4^{-2}/Cl^- ratios **(in milliequivalents per liter, log scale)** for all analyzed water samples **(Figure 3)**. It is obvious that shallow groundwater and deep groundwater plot along two distinct lines. This is further justified by demonstrating the trend of Cl^- concentrations versus $\delta^{18}O$ values (in ‰ V-SMOW, linear scale) in shallow and deep groundwater and the local seawater as well as seawater from Doha-Qatar in Gulph Area **[11]**. It may be realized from **Figure 4** that the extrapolated or forecast trend for shallow groundwater samples (with low SO_4^{-2} content) do not fall on the data points for local seawater (or other tropical seawater from Doha/Qatar). However, the extrapolated or forecast trend for deep groundwater samples (with high SO_4^{-2} and Cl^- contents and enriched $\delta^{18}O$ values) falls in the vicinity of the data points for local seawater (or other tropical seawater from Doha/Qatar). This observation strengthens the possibilities of seawater intrusion in the coastal zone and existence of trapped seawater salinity/build-up of salt-water up-coning in the deep confined aquifer in coastal Karachi.

7. Conclusion

The studies carried out during three year of the project on conjunctive use of stable isotope techniques and conventional non-nuclear techniques have successfully facilitated a general view on the stable isotope composition of oxygen, hydrogen and inorganic carbon in water and its dissolved inorganic carbon as well as hydrochemistry /salinity and biological pollution of potable groundwater system in coastal Karachi. The conclusions on possibilities of seawater and/or existence of trapped seawater salinity/build-up of salt-water up-coning in the deep confined aquifer in coastal Karachi require detail sampling.

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Figure-1: Map of Karachi showing sampling location

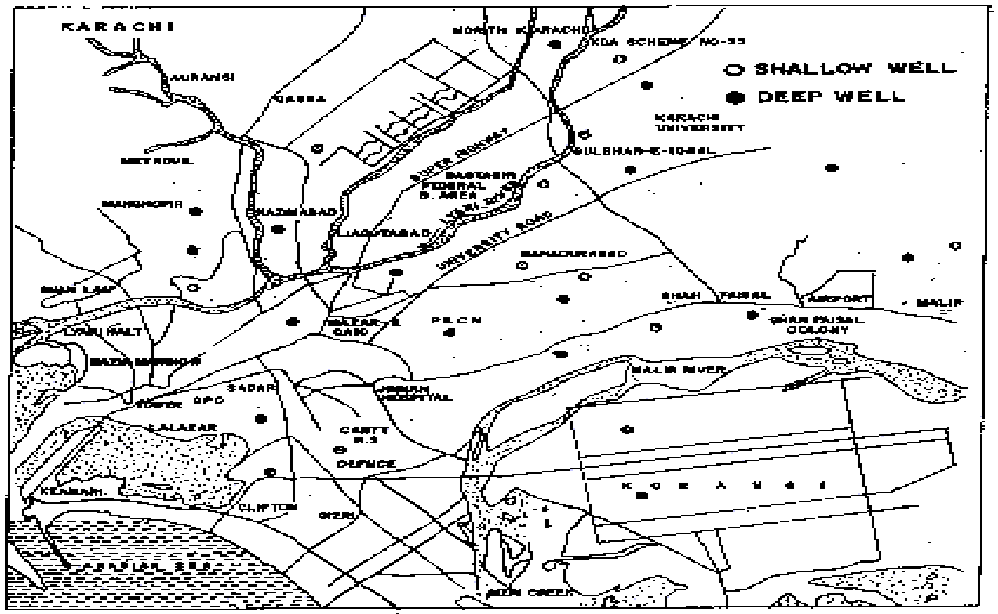

Figure-2: $\delta^{18}O$ versus $\delta^{2}H$ plot of groundwater in coastal Karachi

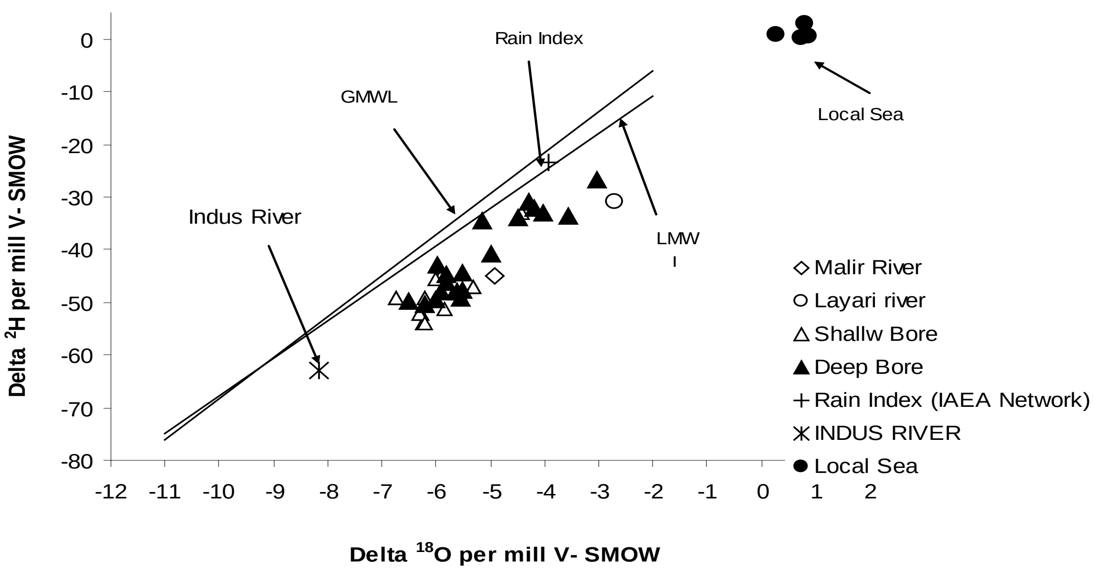

Figure-3 : SO_4 Verus SO_4^{-2}/Cl^- ratios in Karachi groundwater

Figure-4: Chloride versus Oxygen-18 in coastal Karachi groundwater