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CHEMICAL ASSESSMENT OF NATURAL SPRINGS OF SINDH PAKISTAN

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ABSTRACT

The focus of the field study reported here are the water quality issues of twenty four natural springs located in Karachi, Thatta, Jamshoro and Tharparkar districts of the province of Sindh, Pakistan. The samples collected from these springs were analyzed for water temperature, electrical conductance, TDS, salinity and pH and major cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) and anions (Cl^-, HCO_3^-, SO_4^{2-}) by electric probe, flame atomic absorption spectroscopy, uv/visible spectrometric and volumetric methods. A paired t-test was used to assess 24 pre- and post-sampling data during the period 2000 - 2001. The order of relative abundance was detected for major cations was $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and anions $Cl^- > HCO^{3-} > SO_4^{2-}$. The values of positive correlation in the number of pairs showed the origin of transport from same lithology. The factor analysis (FA) was applied to water quality and the first two factors identified were responsible for approximately 80% of total variance. The hierarchical cluster analysis was made using the ward method for group relationship and Pearson correlation coefficient derived for parametric relationship, percent sodium (% Sodium), Langelier saturation index (LSI), sodium adsorption ratio (SAR), residual sodium carbonate (RSC), and permeability index (PI) were made for quality of data and identifying the suitability of water for drinking, industrial and agricultural purposes. The residual sodium carbonate and sodium adsorption ratio indicated for more than 75% springs, were suitable for irrigation purposes.
The spring water showed spatial variations among physico-chemical parameters and results were compared with WHO guidelines for drinking water.

Keywords: Sindh, springs, salinity, water quality, chemical assessment.

INTRODUCTON

The springs are natural escapade of water flow from ground to the earth's surface, instead of a dug well. It seems to be valuable but the quality is questioned. Water quality is important for health and economic development; chemical composition of water varies with reasons, anthropogenic influences and natural processes Simeonov *et al.* (2003). The spring water was classified in different types depending upon the composition of major ions HCO_3^- , Cl^-, SO_4^{2-}, SiO_2 , Na^+, K^+, Ca^{2+} and Mg^{2+}, mainly originated from dissolution or mineralization of rocks (Davisson *et al*., 1994; Afsin *et al*., 2006).

In the context of springs, these natural waters are more concentrated in areas where there have been volcanic activity in recent ages or the past. The quality determined was found rich in sodium by Risenhoover and Peterson (1986), the condition is often accompanied by high levels of calcium 3135 mg/L (Bechtold, 1996), chloride 5500 mg/L by Otero and Soler (2002), bicarbonate 570 mg/L from Howari *et al.* (2005) and certain levels of potassium 2200 mg/L reported by Marie and Vengosh (2001).

Natural mineral water is characterized by its salts content, trace elements or other constituents and where appropriate, by certain effects; also, by being in its original state; both the conditions have been preserved from all risk of pollution. The composition, temperature and other essential characteristics of water of underground origin must remain stable at source within the limits of natural fluctuation; and may not be affected by possible variations in the rate of flow. (Misund *et al.,* 1999; Baba *et al.,* 2008). Salts, sulphur compounds, and other compounds are among the substances that can be dissolved in the water. These minerals have various effects on the health of a person (Burton and Cornhill, 1977; Burton *et al.,* 1980; Epstein and Zavon, 1974). The management and conservation strategies for cold water springs has been reported by Jose Barquin and Mike Scarsbrook (2008). Reimann and de Caritat (1998) have reported natural concentrations in water from different parts of the world. The springs, other than in Sindh province of Pakistan have been studied e.g by Waring (1965) for general characteristics of temperature, flow and associated rocks. Manzoor *et al.* (2002) assessed reservoir

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temperature of thermal springs in northern areas of Pakistan by isotope geothermometry. Farida–Hewitt (1998) contributed her work on spring at Karakorum as a source of water in scarce and its therapeutics. The Shah and Danishwar (2003) studied fluoride in spring water in Naranji area. Whereas Hussain *et al.* (2010) determined springs water quality of Samahni valley for biological life, temperature and pH. However boron contaminations in spring water of Neelum valley was studied by Akram *et al.* (2011). Todaka *et al.* (1999) reported on geothermal characteristics of hot springs of Karachi. Javed *et al.* (2009) highlighted balneology considerations of mineral springs of Manghopir, Karachi. Physicochemical and biological assessment of some springs from Sindh have been reported by Jahangir *et al.* (2001) and Leghari *et al.* (2005, 2006). The objectives of present work is to report comparative studies of springs for chemical assessment and to highlight these valuable asset to academia, consumers, policy makers for better management to maintain quality of drinking, agriculture, tourism and therapeutics of springs in the region. Most of these springs were not reported earlier other than this laboratory. In this study water of 24 springs were collected at different interval during 2000-2001, the locations are showed in figure 1. The results obtained are compared with permissible limits for drinking, livestock management and irrigation purposes to evaluate the natural resources available.

MATERIALS AND METHODS

The representative sample of spring water was collected from each location in cleaned plastic or glass container. The sampling bottles were rinsed several times ≥3 with sampling water prior to sample collection (APHA, 2005). Temperatures of air 1 m above surface water and water were measured by immersing mercury thermometer in the source. The conductivity, salinity and total dissolved solids were estimated with Orion 115 conductivity meter in the field and pH was recorded with Orion 420A pH meter in the laboratory. In meantime the collected samples were stored in cool box, transported to laboratory and filtered if necessary through 0.45µm membrane and analyzed immediately following the protocol of standard

Fig. 1. Springs indicated in map of Sindh and province location in Pakistan along neighboring countries (Source: Google Earth).

methods (APHA, 1992). A portion of fifty milliliter of water was preserved by 2ml 10% HCl and was analyzed within 30 days for sodium, potassium, calcium and magnesium by air acetylene flame atomic absorption spectrometer at 589.0, 766.5, 422.7 and 285.2 nm respectively at the conditions recommended by the manufacturer (Varian Spectr AA-20, Australia). The analysis was carried out in triplicate (n=3) with integration time 3 sec and delay time 3 sec. Five different concentrations of elemental solution were used to establish a calibration curve from standard salts and earlier of this standardized with primary salts. All standard methods of titrimetric, spectrophotometric and atomic absorption spectrometry were applied and standardized for valid data collection. The total hardness was measured by titration with ethylenediamine tetraacetic acid disodium salt using erichrome black T as indicator at pH 10 (APHA, 2005). Total alkalinity was determined by hydrochloric acid titration using methyl-orange as indicator for endpoint and chloride was analyzed by silver nitrate ($AgNO_3$) titrant using potassium chromate (K_2CrO_4) solution as an indicator. Sulphate was determined at acidic pH by spectrophotometrically using barium sulphate turbiditimetric method (APHA, 1992).

Geography of the study area

Sindh is located at the western corner of south asia, geographically Sindh province is third largest in size and second most populated in Pakistan, stretching about 579 km from north to south and 442 km (extreme) or 281 km (average) from east to west, with an area of 140,915km^2. The province may be regarded as a low and flat, Most of springs exist in the hilly areas from south west of central to lower Sindh and ends within coastal areas of Thatta and Karachi. Although most of the springs are scattered in arid region, localities are benefited from these valued springs (Table 1). Sindh province is situated in a subtropical region; hot in the summer and cold in winter. Temperatures frequently rise above 46°C between May-August and minimum average temperature of 22°C occurs during December and January. The annual rainfall reported by Pakistan Meteorological Department (2011) averages 400 mm, mainly during July and August since 1971-2000. The southwest monsoon wind begins to blow in mid- February and continues until the end of September whereas the cool northerly wind blows during winter months from October to January. There are no surface water resources to recharge aquifers, other than annual precipitation within the study area. Due to

Table 1. Description of springs, location and discharge flow.

S. Id.	Sampling Stations	Location (GPS)	Description of sampling stations	Discharge flow
St.1	Manghopir I	24°59'16.5"N 67°02'34.4"E	Spring inside Hall, located at north west of Karachi city, Size of spring length 40, width 5 and depth 5 feet (altitude 259ft.),separate bath for men and women	The water receipt, discharge balances the amount withdrawn
St.2	Manghopir II	24°59'17.0"N 67°02'34.1"E	Hot spring open well bath of length 2, width 3 and depth 4 feet.	do
St.3	Manghopir III	24°59'14.9"N 67°02'36.7"E	Size of spring 4 ft each of width and depth (Altitude 288ft), located in south east of about 20-30 m from St.1 and St.2	do
St.4	Manghopir IV	24°58'47.9"N 67°02'05.6"E	A pond about 50feet long, 40feet wide and with the depth of 5feet. (Altitude 224ft.) The surface of earth is rocky and there are some trees inside. A number of crocodiles inhabit in the pond. Open view by grill and a gate.	The pond is perennial and water oozes from bottom.
St.5	Abdullah Shah Ghazi	24°48'36.9"N 67°01'49.6"E	It has dimensions of 10 x 10 feet with depth of 2 to 3feet. (Altitude -47ft).	The water receipt, discharge balances the amount withdrawn.
St.6	Shree Ratneshwar	24°48'45.8"N 67°01'36.9"E	The spring is located in natural depression in a cave at the foot of tomb in south within a constructed area. It is 1Km far from sea beach Clifton and about 500m far from spring Abdullah Shah Ghazi, Karachi (St.5). (Altitude -39ft)	do

Continued…

nonavailability of the surface water, groundwater is mostly used to meet all water requirements.

Geology of the study area

Pakistan is spread along in contact between the Indian and Eurasian plates and is situated in the north western corner of the Indian plate. To its south-east is indian plate and to the north the Asian/Karakorum continental plate. Tertiary units of the western fold belt comprises mainly Sulaiman, Khirthar and Pab and are variety of regional names (Hemphill and Kidwai, 1973; Shah, 1977) and correlation between regions and dating is at a reconnaissance level. The Sulaiman and Khirthar formations include early to mid eocene rocks of Ghazi and Khirthar marine shelf facies. These are overlain by marine facies of the oligocene Nari formation and miocene Gaj formation Smewing *et al.* (2002). The Khirthar mountains extend to the south east ward curving for about 240km from northwestern extremity of Sindh Mirjat *et al.* (2011). The northern half of the range is flanked by sharp hills

Table 1. continued…

S. Id.	Sampling Stations	Location (GPS)	Description of sampling stations	Discharge flow
St.7	Baba Bukhari	24°52'36.8"N 67°01'36.9"E	It is located on Shahrah–e– Faisal (Airport road), approximately 4km from Drigh road railway station. Bath for men and women. The water pool measured for length and width of 12 ft and depth 3feet. (Altitude 77ft.)	28L/ Sec
St.8	Dhabeji I	24°50'07.9"N 67°06'06.6"E	It is located near tomb of Baba Bukhari, Dhabeji, district Thatta	3-4L/min
St.9	Dhabeji II	-	This is located about 3 Km from the east of the Dhabeji railway station with Size of 4x6feet and water depth of 1 to 2feet	5-6L/Sec
St.10	Gharo I	24°25'07.9"N 67°31'20.3"E	Spring located eastern side of Bhambhore bridge, district Thatta	1L/Sec. (Apparent at low tide)
St.11	Gharo II	-	Spring located western side of Bhambhore bridge	5L/Sec. (Apparent at low tide)
St.12	Rannikot I	25°53'54.5"N 67°52'49.1"E	A main spring at Mohn gate, 30Km in the west from Indus highway from the town Sunn, district Jamshoro	70 L/Sec.
St.13	Rannikot II	-	A natural pool, near Merrikot lower.	The water receipt, discharge balances the amount withdrawn.
St.14	Rannikot III	-	Natural pool near Sunn gate, fort entrance.	do
St.15	Lal Bagh I	-	200-300m far from east side of Lal Bagh graveyard located 2 Km from Sehwen city and 0.5Km from Indus highway district Jamshoro	do
St.16	Lal Bagh II	-	The constructed pond in a cubical shape, about 50m far from spring I, used for drinking and bathing separately for men and women	do
St.17	Lakhi Shah Saddar I	26°16'50.98" N, 67°50'41.33"E	About 20 x 12 feet with depth o f 2 to 3 feet (Altitude 260ft), district Jamshoro	7 L/Sec.
St.18	Lakhi Shah Saddar II	-	About 200m north of main spring (St.17), at a small distance appears as pool of about 14 x 8 feet with depth about 1 to 1.5 feet (Altitude 258ft).	4 L/Sec.

Continued…

Table 1. continued…

S. Id.	Sampling Stations	Location (GPS)	Description of sampling stations	Discharge flow
St.19	Lakhi Shah Saddar III	-	Located of 2-3km from main hot spring (St.18) in the southwest within the same valley and appears as a small pool of about 2 x 2 feet with a depth of about 0 .5 ft. (Altitude 150 ft).	0.5 L/min.
St.20	Ghazi Shah	26.25N, 67.30E	Escape opening of about 7.5 feet wide and 9 feet height with water depth of 1.5 feet. (Altitude 500ft). Spring is about 32Km in south west of Johi town, 4Km from village Ghazi Shah, Taluka Johi, district Dadu	3 L/Sec.
St.21	Kai	26.25N, 67.42E	Size of 20 x 25 feet with water depth of about 6 to 8 ft About 40 Km west of Sehwan and 25 km from Jhanghara village, Taluka Sehwen, district Jamshoro	1 L /Sec.
St.22	Thoba	-	Natural pond at village Loni about 8km far from Jhangara, Taluka Sehwen	-
St.23	Khumb	-	Stream about 15km from Jhangara, Taluka Sehwen	-
St.24	Inchaile Sir	24.25N, 70.40E	Spring located to 1km from Nagarparkar town , district Mithi	2 L/min.

do =The water receipt discharge, balances the amount withdrawn
- = Not available

developed on the tertiary Nari series, overlying them to the east is the Gaj group. In geological map of Pakistan (Fig. 2) Sindh have been indicated and classified with four important geological characteristics e.g quaternary, tertiary recent, late mesozoic and tertiary marine shell sediments and are represented vertically. The geological time scale is divided in three main eras, they gradually become older in order of cenozoic, mesozoic and paleozoic. The quaternary and tertiary epochs are among of cenozoic era and the mesozoic eras are indicated in the figure 2 and the geology is explained following in three regions.

Karachi region: The two formations are continuously exposed from the western coast of Karachi to northern Sindh. These exposed rocks are Nari and Gaj formations of oligocene (tertiary) and miocene age (quaternary) respectively (Fig. 2). The Nari and Gaj formations consist of limestones, shales and sandstones which are divided into several smaller units Shahid *et al.* (1996). Nari formation predominantly consists of greenish gray, brown to buff colored, fine to coarse grained, massive, cross bedded sandstones. Occasionally conglomeratic and calcareous in nature. The division is widely exposed on the lower slopes of eastern Khirthar range in low grounds of Thana Bola Khan up to Jungshahi. The Gaj formation is mainly composed of calcareous sandstone and limestone interbedded with shale. The sandstone is soft, fine grained and yellowish brown to gray in color. Occasionally the limestone is cream colored when fresh but brown when weathered (Farshori, 1972). A number of springs were found in Karachi and Thatta districts from St.1to St-11. Some of the hot springs were found in faults and are shown in a conceptional model of Karachi geothermal system by Munawar (2009) (see Fig. 3).

Dadu and Jamshoro region: The lakhi springs of eocene within lakhi range (Table 2) is mainly composed of tertiary rocks, the north south thrust fault of lakhi range runs along the eastern flank for most of 35 miles from Lakhi Shah Saddar to Rannikot fort and seems to extend further southward (Farshori, 1972). The samples St.17-19 were collected from lakhi range (Fig.1). The rannikot group is named after the Rannikot fort in laki range and is in paleocene age with its lithological characteristics of yellowish brown sandstone and shale interbedded with limestone. The upper contact of the group with ghazij formation and lower contact with pab formation are conformable Blandford (1876). The samples St.12-14 were collected from the rannikot fortress and St.19-23 from the same region are shown in figure 1.

Thar region: The whole area is covered with extensively thick cover of sands dunes, extending down to an average depth of 80m. Surface rock exposures are almost absent, except limited outcrops of granitic basement in Nagarparkar. A few scattered outcrops of mesozoic and tertiary strata are exposed across the Indo-Pakistan border. Thar desert rests upon a structural platform where granitic basement is at shallower depths Zaigham and Ahmed (1996). The granite basement has pre-jurassic rifting, which caused flexure and the ultimate development of the Thar basin. The basement shows rise towards southeast and deepening towards northwest, as a result of paleozoic-mesozoic divergent tectonics. The consistent trends of the stratigraphic sequences from mesozoic to tertiary periods indicate that the incipient rifting of the basement was pre-depositional. The younger formations

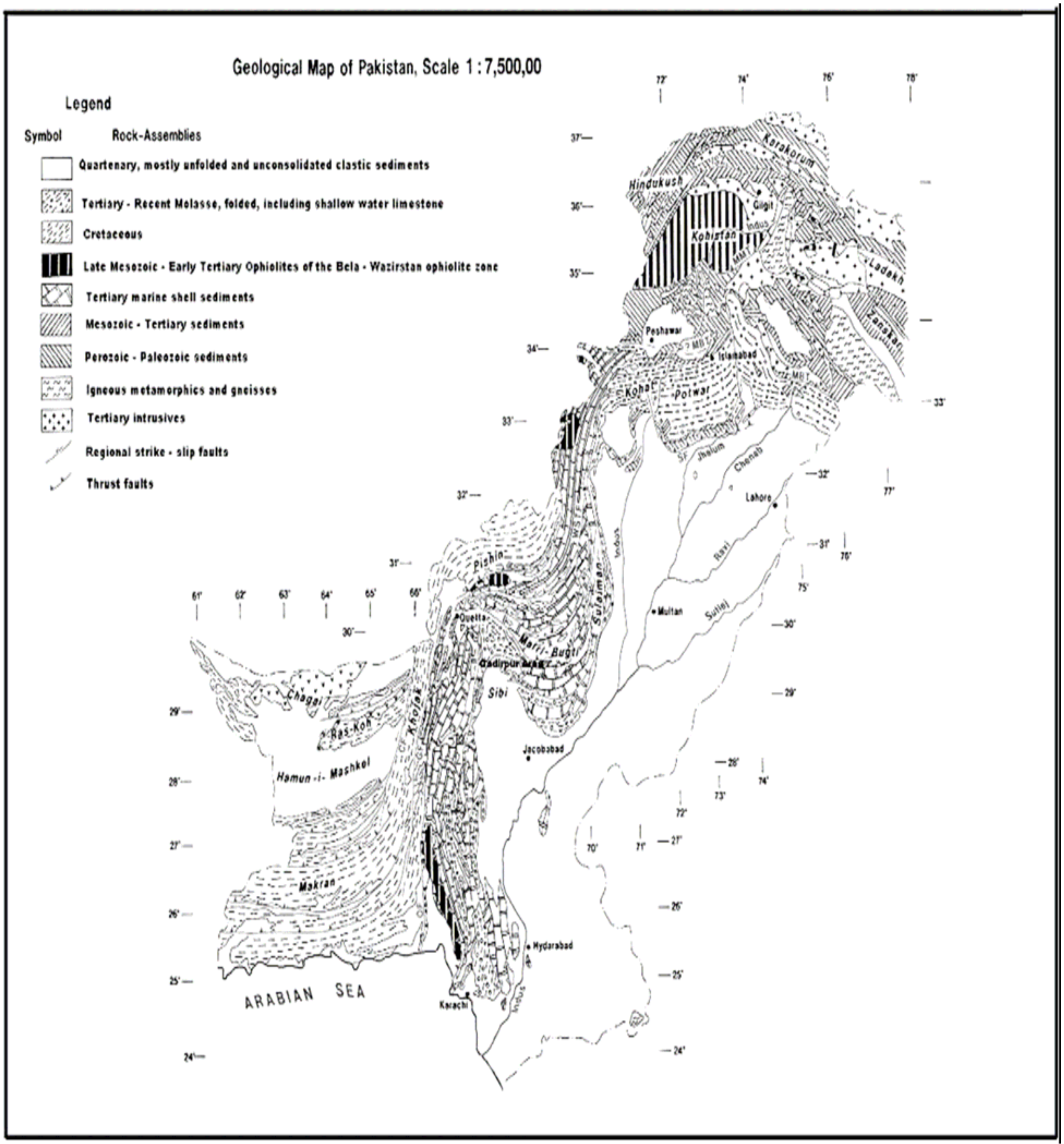

Fig. 2. Geological Map of Pakistan adopted from Bender and Raza, 1995.

Table 2. Stratigraphy of Southern Indus basin, Pakistan (adopted from Shah, 1977; Dolan, 1990).

Depth to Formation (m)	Stratigraphic unit	Age	Dominant Lithology
5	Lakhi Formation	Eocene	Limestone
95	Rannikot group (Lakhara F.)	Paleocene	Sandstone , gray shale
888	Rannikot group (Bara F.)	Paleocene	Sandstone, gray shale, basalt
888	Rannikot group (Kadro F.)	Paleocene	-
1035	Pab Sandstone	Late Cretaceous	Sandstone, brown shale

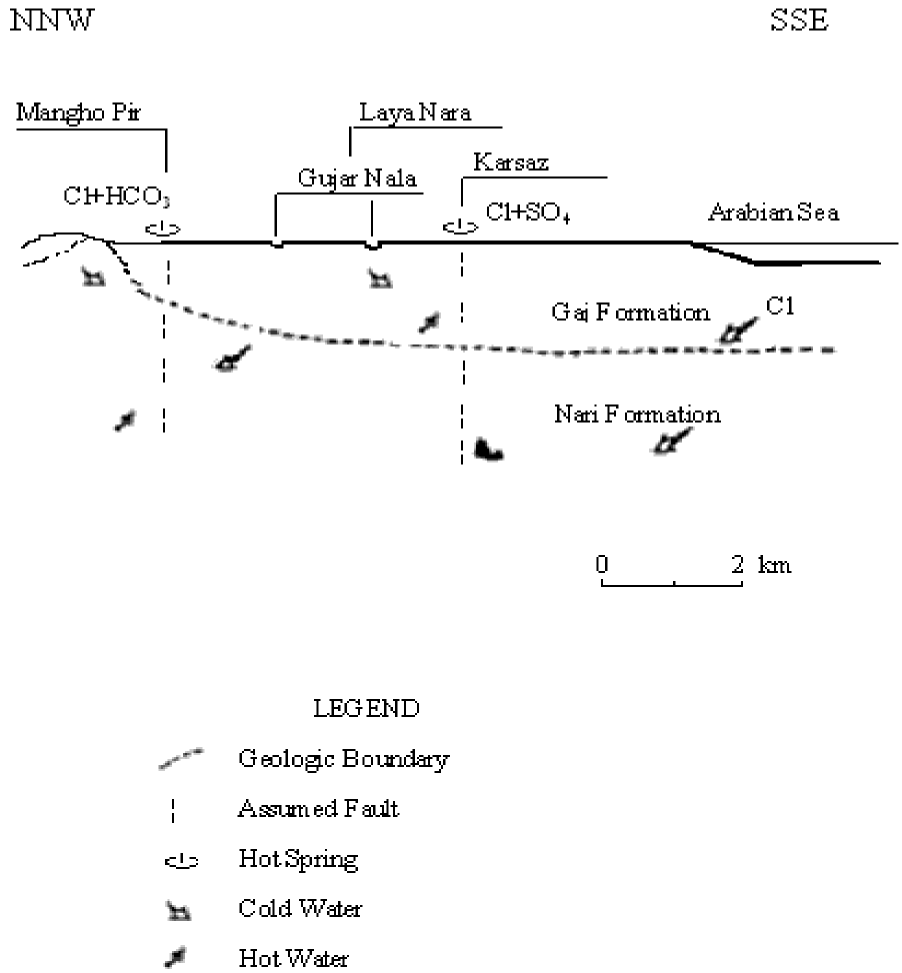

Fig. 3. Conceptional model of Karachi geothermal system by Munawar (2009).

are preserved and overlie the older in the northwestern part, where geological sequences are well developed. The older formations may be encountered at greater depths towards the basin and shallower on the continental shelf area towards southeast (Zaigham, 2002). The hydrogeology of Thar desert explained (Zaigham, 2002) for the ground water tapped by 83% of dug wells has an electrical conductivity (EC) value ranging from 2000µS/cm to more than 10,000µS/cm. In the central part, south and southeast of Chachro extending from Pakistan-India border to Islamkot, EC values are between 2,000 and 5,000µS/cm were particularly in the relatively deeper aquifer(s). The EC values ranging from less than 2,000 to 3,000µS/cm in and around Nagarparkar, where the basement units are exposed. The spring Inchile sir (St.24) is sampled 1 km far from Nagarparkar town.

RESULTS

Groundwater quality classification

The spring water is most probably a representative of groundwater quality a number of spring water samples (24) were collected and their results are given in table 5 along with the samples description provided in table 3. The geochemistry of ground can be represented by plotting the concentrations of major cations and anions in

Table 3. Physico chemical parameters of springs (in mg/L, pH unitless) of Sindh.

S. Id	Sampling Station	pH	EC µS/cm	Sal. g/L	TDS	T Alk.	Har.	Ca	Mg	Sulphate	Water °C	Na	K	Cl
1	Manghopir I	7.74	2630	1.15	1683	250	175	34	28	206	45	350	13	387
2	Manghopir II	7.75	2670	1.15	1708	297	180	39	32	211	46	373	16	441
3	Manghopir III	7.45	3212	1.5	2105	307	265	97	60	118	47	440	24	556
4	Manghopir IV	7.1	4300	2.35	2752	435	335	196	41	332	26	340	15	905
5	Abdullah S Ghazi	7.5	4165	1.35	2666	467	326	117	78	322	30	491	58	554
6	Shree Ratneshwar	7.8	4185	2.25	2678	367	241	52	42	238	28	395	43	461
7	Baba Bukhari	7.4	8415	4.63	5474	331	596	283	141	342	35	693	105	1250
8	Dhabeji I	7.3	3101	1.5	1984	163	470	108	49	ND	30	342	16	702
9	Dhabeji II	7.5	4136	1.95	2646	110	580	77	56	ND	30	394	23	750
10	Gharo I	7.1	3897	2.1	2494	392	767	174	91	196	26	592	20	861
11	GharoII	7.1	3774	2	2415	413	717	177	65	196	26	446	21	835
12	Ranikot I	7.8	1217	0.5	779	205	292	95	39	112	28	132	18	296
13	Ranikot II	7.9	2500	1.1	1601	240	495	151	71	129	27	211	21	545
14	Ranikot III	7.7	3150	1.25	2015	243	690	176	88	146	26	315	31	782
15	Lal Bagh I	7.7	2301	1.35	1472	108	383	96	53	212	32	184	27	281
16	Lal Bagh II	7.34	2417	1.3	1545	125	390	105	55	225	31	194	32	310
17	Lakhi Shah Saddar I	6.78	13100	7.2	8384	242	612	304	139	871	40	1787	76	3560
18	Lakhi Shah Saddar II	6.6	14160	7.4	9062	236	672	315	177	969	42	1998	78	4266
19	Lakhi Shah Saddar III	7.2	1760	1.15	1126	112	126	76	23	127	32	158	58	150
20	Ghazi Shah	7.2	1079	0.25	690	115	207	43	25	ND	39	51	9	161
21	Kai	8.1	887	0.2	567	82	167	38	18	ND	35	54	7	111
22	Thoba	7.9	3515	1.65	2249	193	332	125	71	223	26	362	27	781
23	Khumb	7.5	3163	1.45	2025	157	472	91	43	127	29	301	22	593
24	Inchaile Sir	7.2	1452	0.9	946	234	277	78	42	128	29	112	17	273
	*WHO (2004)	6.5-8.5	-	-	100	120	200	75	30	250	-	200	24	250
	t-test paired	-2.03	0.87	2.41	0.93	-.94	0.79	1.80	1.81	2.86	2.56	1.52	1.83	0.68

ND= Not determined, - = Not decided

diagram from the Piper (1953). Aquachem software was used for developing the piper diagram (Fig. 4) and was used to portray principal hydrochemical compositional features in two parallel triangles along with diamond to top in a figure. The elements grouped in Na, K, Ca, Mg and HCO_3, SO_4, Cl developed in a trilinear diagram and showed the nature of springs water of sodium-potassium chloride (Na-KCl) and calcium-magnesium chloride (Ca-MgCl). The diagram showed predominance of cation evolved from Na+Ca to Mg-K and predominance of anion from Cl^- towards HCO_3 or SO_4.

The concentration of Na+K had indicated (triangle in left for cations) more than 50% for each in many of 24 springs, inversely most of samples showed lower concentration (50%) for Ca+Mg. The right side of triangle represented approximately all of springs were rich in chloride and found within 70-100%. The lower concentration of bicarbonate against the chloride, which did not exceeding greater than 30%. The $Cl+SO_4$ and Ca+Mg were found at both sides simultaneously, when judged the head of arrows raised upward within diamond shape (a blend of cations and anions). The $Cl+ SO_4$ indicated for almost all of samples lying within 75-100% with high concentration of anions. The scale for Ca+Mg indicated most of samples lower than 50% of concentration. Inverse to Ca+Mg the Na+ K had indicated more than half of springs rich in these concentrations and found more than 50%. The bicarbonate showed similar patterns as was found in triangle for the anions.

It can be readily seen (Table 4) that only two types of source springs were found, one of which is relatively rich in $NaCl/HCO_3$ and was indicated in many of samples St.1-6,10-14, 22, 23 and St.24. Whereas, the other type of source water was rich in $NaCl/SO_4$ for St.7, 15-18 and St. 19.

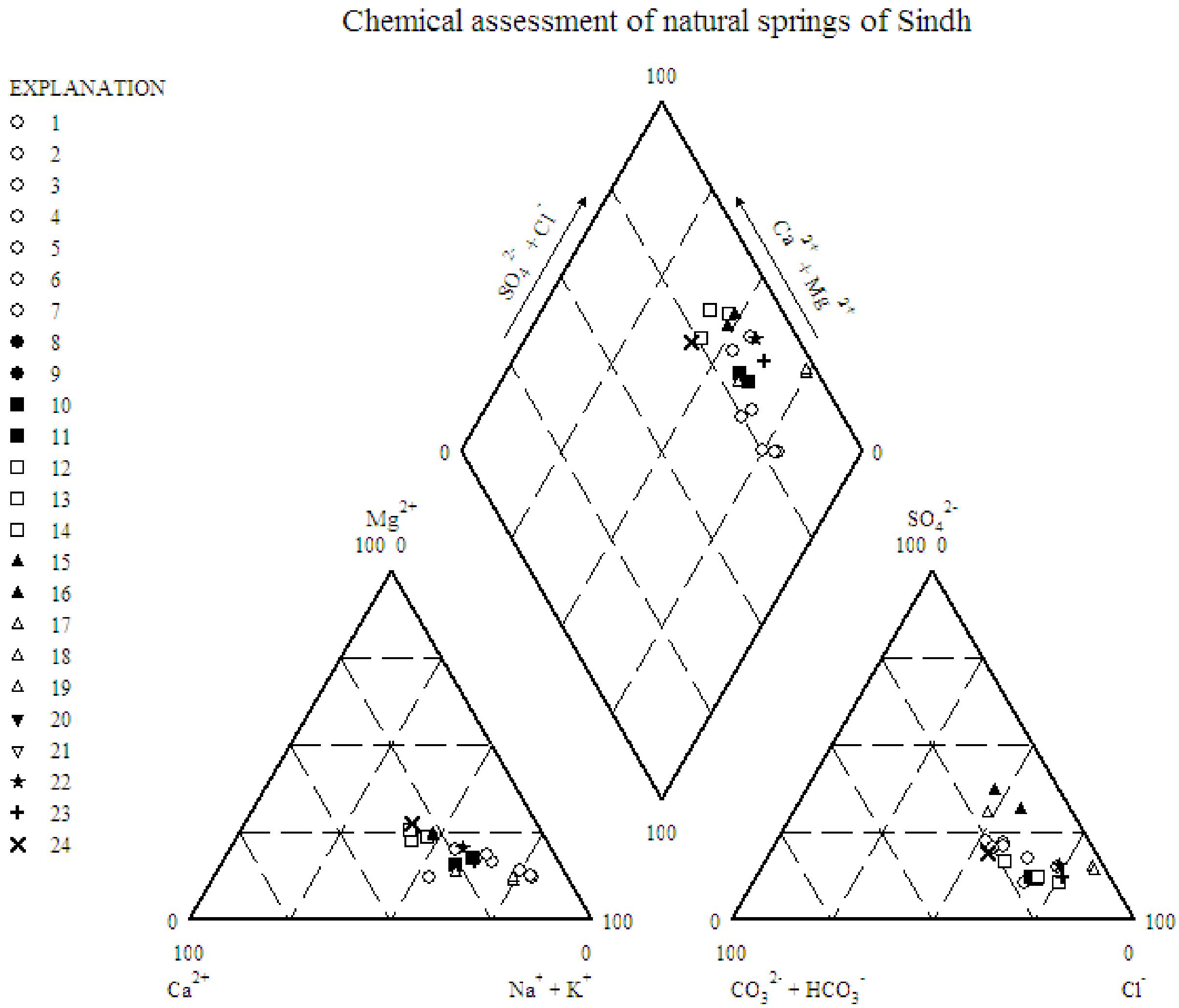

Fig. 4. Piper diagram showing water type of springs.

Statistical Analysis

The computer program Excel 2003 (Microsoft Office®) and SPSS 16 (SPSS Inc., Chicago, IL, USA) were used for results validation, data reduction and cluster analysis. Table 4 indicated each variable with standard deviation and standard error for thirteen physicochemical parameters and paired t test at degree of freedom 23 using t-distribution table and is indicated for most of variables below 1.7. The accuracy and precision of chemical data was validated from ionic charge balance error in milliequivalent adopted earlier by Lloyd and Heathcote (1985). After processing the data, all of the samples were found within acceptable limit maximum up to 10 percent (Fig. 8).

The ratio of total anions to that of cations ((anions)/(cations)) was an indicator for completeness of measured parameters Mouli *et al.* (2005) and the scatter plot linear regression to sum of cations and anions in milli equivalent obtained r^2=0.9635 and indicated that the quality of data was good. Langelier saturation index (LSI) scale is commonly between -3 to 3 which was developed for predicting (Langelier, 1946) the degree of corrosion. The negative LSI values indicate unsaturation and potential to dissolve more salts. The number of springs distributed in three categories, the category 1 indicated samples St.18, St.19 and St.20 of negative LSI -0.00061, -0.084 and -0.18 respectively and these waters caused slight corrosion with non scaling. The five of springs St.8, St.9, St.10, St.23 and St.24 fell in corrosive nature, considered in category two and most of remaining (13 nos.) springs are comprised over in category three of range >0.5-2 and thus indicated to scale forming but non corrosive.

Residual sodium carbonate (WHO, 1989) is a measure of higher concentration of carbonate and bicarbonate in relation to calcium and magnesium and alternatively this influences suitability for irrigation. The excess quantities of sodium bicarbonate and carbonate cause dissolution of organic matter in soil. Here we determined for 24 samples (Fig. 9), 18 samples indicated in safe rating (<1.25) with 75 percent of its credit, five springs (21%) were within marginal range (1.25-2.50) and only one spring was unsuitable (>2.50 for irrigation or plants).

Investigations of springs water for drinking and irrigation
The half of total spring discharges its water from source with flow rate of 0.5-7L/Sec, hence depending upon quality these waters are used for irrigation and drinking purposes. The two of springs from Rannikot and Baba Bukhari Karsaz having high flow of 70 and 28L/Sec respectively. The quality of spring in latter is not suitable for drinking and the flow disappears within the cracks of rock soil after exposure to some distance. The water of Rannikot is used for irrigation and drinking purposes by the population within hilly area. Two of springs with flow of 1-5L/Sec at the bank of Gharo creek discharges its water directly into the marine tides. The quality of this water is not suitable for drinking but could be used within salt tolerant irrigation. Among all the twenty four springs, only two samples of lakhi I and II showed high salinity and could not be recommended for drinking, livestock and poultry purposes (Ayers and Westcot, 1986). High concentrations of exchangeable (soluble) sodium and high levels of salts in soils negatively affect the plant growth. Soils with high exchangeable Na have poor tillage qualities and permeability. The sodium adsorption ratio (SAR) is more representative for the quality, which compares the concentrations of Na, Ca and Mg in irrigation waters. Since Ca and Mg bring moderate decline in the negative effects of Na, the salty taste of water is not that much as it should be. The SAR scale is adoptable for crop yield and nature of crop. The sodium adsorption ratio (SAR) is based on milliequivalent for classification of irrigation water. The spring water was classified on basis of sodium adsorption ratio (WHO, 1989) for detecting suitability of water for irrigation. It was admitted in majority of twenty springs with 92% share were in good category (<7) and only two of water samples found unacceptable (>7) for irrigation (Fig.10).

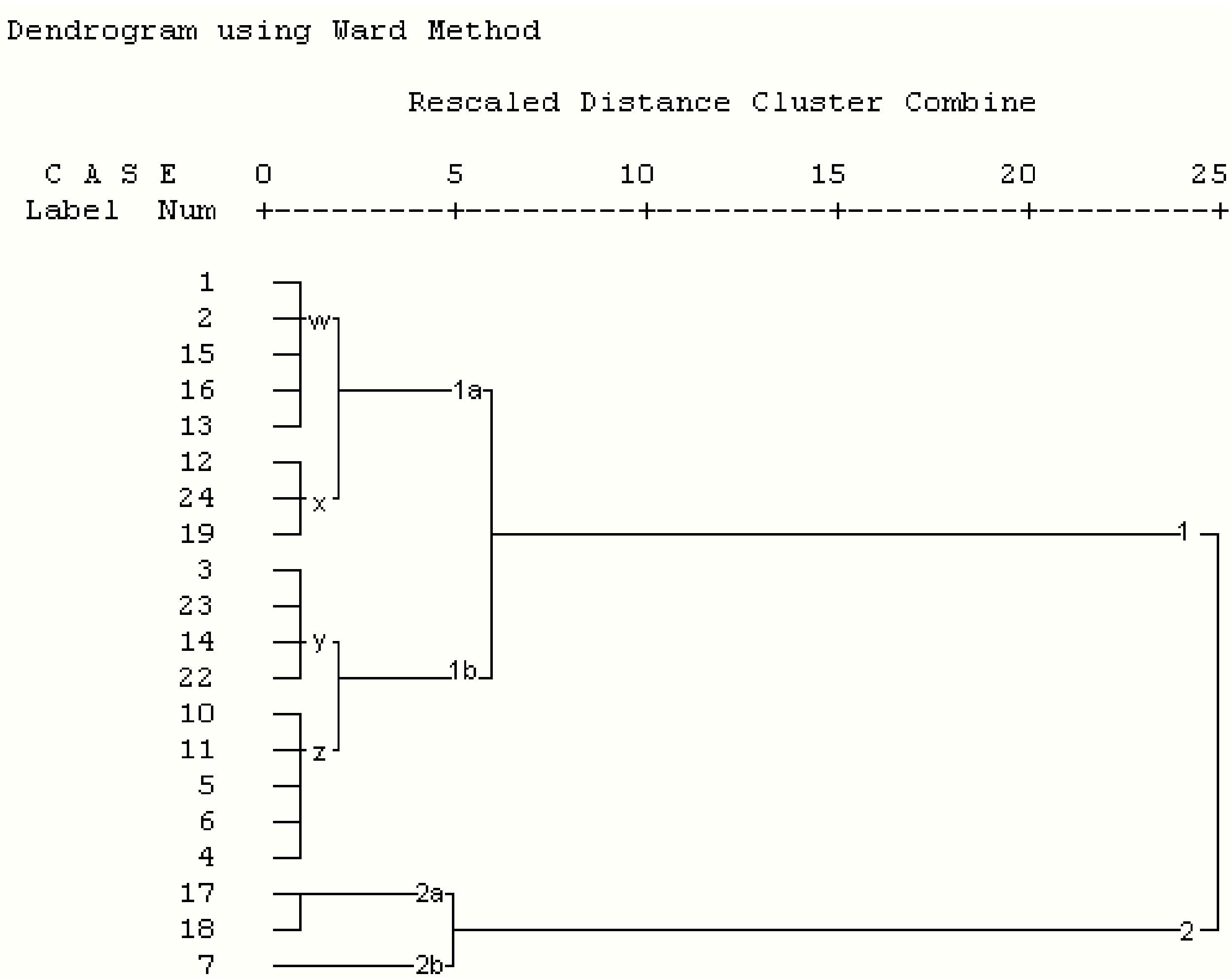

Fig. 5. Dendrogram showing Clusters among springs.

Conductivity is another measure of irrigation water quality, and the measured conductivity in the field can be used as a measure of salinity. Lloyd and Heathcote (1985) suggest that a conductivity measurement of <250 µS/cm is of low salinity, with no detrimental effects on crops expected, 250 to 750 µS/cm represents medium salinity, with detrimental effects to sensitive crops expected, 750 to 2250 µS/cm represents high salinity, with adverse effects on many crops., and 2250 to 5000 µS/cm represents very high salinity, suitable only for salt-tolerant plants (Table 3). The nineteen springs out of twenty four indicated were with high salinity water.

Cluster analysis (CA)

The hierarchical cluster analysis was applied to detect site similarity in groups between sampling springs using ward method with euclidean distance as a measure of similarity (Fig. 5). Two of statistically significant clusters were formed; Cluster 1 comprised over sets 1a & 1b and these were further lined into subsets. w(St.1, St.2, St.15, St.16, St.13) and x(St.12, St.24, St.19); the y(St.3, St.23, St.14, St.22) and z (St.10, St.11, St.4, St.5). Cluster 2 was divided into two subsets 2a(St.17, St.18) and 2b(St.7). These waters represent to springs of Lakhi Shah Saddar and Baba Bukhari Karsaz. These showed similar characteristic features, natural background and were affected with similar concentrations or type.

Factor Analysis (FA)

The aspect of complexity arises from large number of parameters (Saffran, 2001), factor analysis was used to data reduction, A highly correlated variables were removed with smaller number of uncorrelated variables. It was found that first two eigen values were higher than 1 and these could be seen in the Scree plot (Fig. 6). The eigen values less than one observed for 3rd factor and so, were eliminated on statistical extraction. It was observed that a majority of the total variance of original data has been explained in first two factors. On either of factor rotation (varimax) or unrotated factor loadings (Johnson and Wichem, 2002) the proportion of total variance is explained by first two factors with contribution of variance 80% shown in table 6 and figure 7. The factor 1 is loaded with 68 percent and factor 2 with 12 percent; and remaining 10 components explained only 20%. The factor analysis of first two factors were indicated for water quality parameters of springs in tables 6 and 7.

Bivariate correlation coefficient

Correlation coefficient is bivariate analysis to measure relationship between pairs; it is a dimensionless index, ranging from -1 to +1 to reflect the linearity relationship between two data sets. The correlation matrix's for 13 variables were produced using SPSS, whereas values close to 1 proves strong relationship (Table 8). The EC indicated strong positive correlation with chloride (0.966),

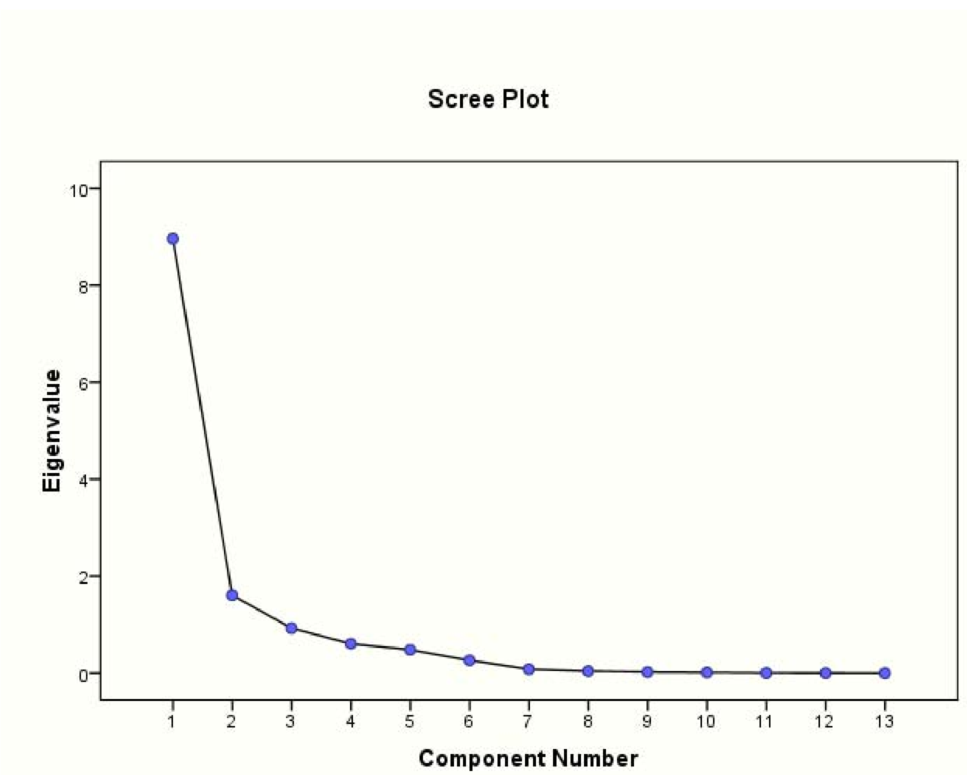

Fig. 6. Scree plot of eigen values against components for springs water quality data.

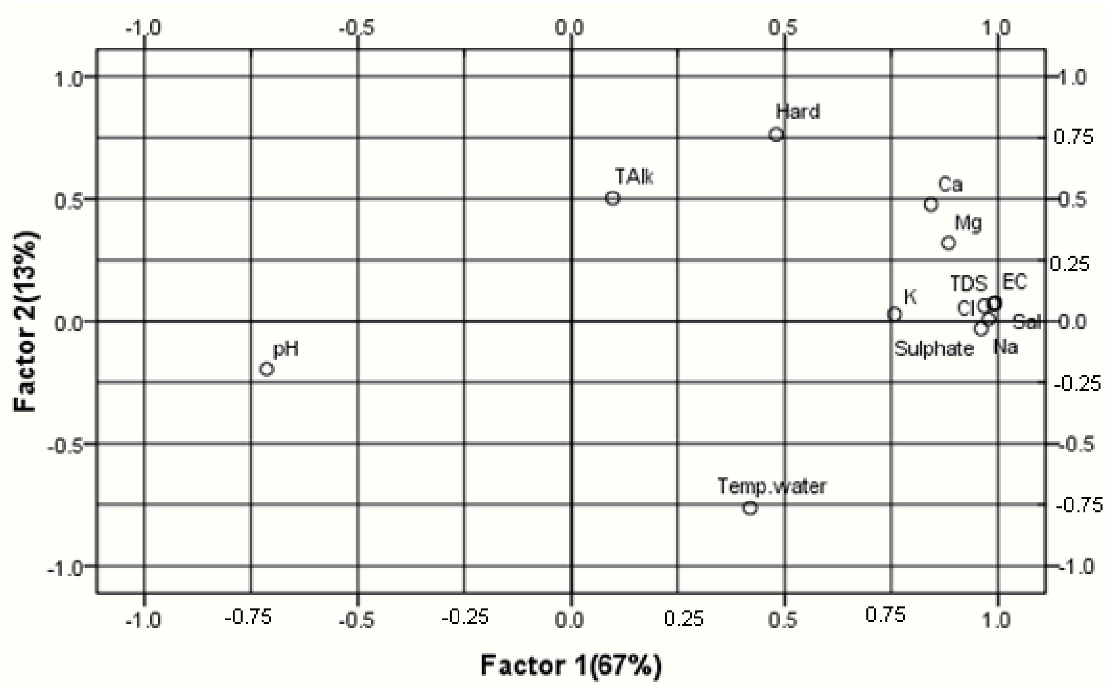

Fig. 7. Factor analysis of springs in Sindh.

magnesium (0.890), calcium (0.851), potassium (0.745) and moderate with hardness (0.516). The hardness represented moderate correlation with chloride (0.535) and sodium (0.496). The sodium indicated its significant positive relationship with EC (0.973), chloride (0.983), magnesium (0.849), calcium (0.781), potassium (0.638) and moderate with hardness (0.496). Chloride showed positive correlation with sodium (0.983), magnesium (0.856), calcium (0.828), potassium (0.602). The metal ions of calcium, magnesium and potassium showed its positive relation with EC 0.851, 0.890, 0.745 respectively. The calcium indicated positive correlation with magnesium (0.911), TDS (0.852), chloride (0.828), sodium (0.781) and potassium (0.664). Magnesium showed its strong positive correlation with calcium (0.911), sodium (0.849), potassium (0.742) and hardness (0.726). The potassium indicated strong positive correlation with magnesium (0.742), calcium (0.664), sodium (0.638) and moderate towards chloride (0.602) and hardness (0.288). It was noticed the pH indicated negative correlation with all chemical parameters and water temperature had proved negative correlation in such pairs.

Multivariate Elemental ratios

When Na and Cl values were plotted, most of samples fall on the 1:1 line with r^2=0.9599, the samples number St.1, St.2, St.3, St.5, St.6, St.10, St.15 and St.19 have slightly higher of Na values compared to chloride, and sample numbers St.4, St.7, St.8, St.9, St.11, St.12, St.13, St.14, St.16, St.17, St.18, St.20, St.21, St.22, St.23 and St.24 have lower Na values when compared to Cl. The Na/Cl ratios of springs were observed close to similar in case of dissolution of pure halite (0.65) which is maintained in solution unless significant cation exchange that reduces Na concentration (Leonard and Ward,1962; Richter and Kreitler, 1991). The series of some more ionic ratios of interest were selected Cl/SO_4, (Na+K)Cl, (Na+K)/(Ca+Mg), Cl/HCO_3 and $(Cl+SO_4)/HCO_3$ and are presented with r^2 values 0.9015, 0.9599, -4.181, -2.466 and -0.652 respectively.

DISCUSSION

The twenty four springs from various locations of Sindh province were collected during study period 2000-2001. The samples descriptions are given in table 1 and the physicochemical parameters of water quality are indicated in table 3. The water temperature ranged between 26-47°C. The highest temperature was found at Manghopir III spring, manually which was entrapped in close constructed hall. In similar to another group of springs were lakhi that showed temperature of 42°C and is classified as “thermal spring”. pH range of springs water was observed within 6.6 to 8.1 and fall in permissible limits of WHO (WHO, 2004) with an average value 7.4. The average minimum and maximum pH values were observed at Kai and Lakhi springs respectively.

The electrical conductivity (EC) and total dissolved salts (TDS) of the springs were within 887-14160 µS/cm and 567-9060 mg/L, with maximum for lakhi spring I and minimum for Kai spring, with an average of EC 3966µS/cm and TDS 2544mg/L (n=24). Only four springs

Table 4. Some quality analysis parameters of springs of Sindh

S. Id.	Sampling stations	LSI	SAR	PI	RSC	% Sodium	Ionic eq. balance percent error	Na/Cl meq./L	SO_4/Cl meq./L	Water-type
1.	Manghopir I	0.63	3.975	92.404	1.32	80.91	9.24	1.39	0.39	NaCl/HCO_3^-
2.	Manghopir II	0.80	3.914	90.968	1.65	79.49	9.99	1.30	0.35	NaCl/HCO_3^-
3.	Manghopir III	0.88	4.067	87.594	0.60	78.09	2.89	1.22	0.15	NaCl/HCO_3^-
4.	Manghopir IV	0.54	3.008	85.171	2.66	71.52	-0.36	0.57	0.27	NaCl/HCO_3^-
5.	Abdullah S Ghazi	0.83	3.800	83.442	1.44	74.31	-5.24	1.36	0.42	NaCl/HCO_3^-
6.	Shree Ratneshwar	0.63	3.70.3	88.099	1.94	77.22	0.34	1.32	-	NaCl/HCO_3^-
7.	Baba Bukhari	0.90	4.988	83.303	-2.51	78.24	1.61	0.85	0.20	NaCl/SO_4^{2-}
8.	Dhabeji I	0.2	3.893	90.059	-0.38	80.73	-2.27	0.75	-	-
9.	Dhabeji II	0.024	4.628	90.555	-1.22	83.81	4.09	0.81	-	-
10.	Gharo I	0.46	4.647	85.430	0.18	77.39	-5.36	1.06	0.16	NaCl/HCO_3^-
11.	GharoII	0.50	3.709	84.920	1.44	74.48	-5.76	0.82	0.17	NaCl/HCO_3^-
12.	Ranikot I	0.78	1.506	82.690	0.44	63.04	-1.89	0.68	0.28	NaCl/HCO_3^-
13.	Ranikot II	1.1	1.988	78.404	-0.52	64.63	-5.19	0.59	0.17	NaCl/HCO_3^-
14.	Ranikot III	0.90	2.782	80.513	-1.18	70.54	-8.84	0.62	0.13	NaCl/HCO_3^-
15.	Lal Bagh I	0.46	2.213	84.088	-1.09	72.71	3.46	1.00	0.55	NaCl/SO_4^{2-}
16.	Lal Bagh II	0.17	2.248	83.822	-1.08	72.45	6.74	0.96	0.53	NaCl/SO_4^{2-}
17.	Lakhi Shah Saddar I	0.16	13.61	93.079	-3.29	90.72	-2.34	0.77	0.18	NaCl/SO_4^{2-}
18.	Lakhi Shah Saddar II	-0.00061	13.97	92.240	-9.94	90.19	-2.32	1.63	0.62	NaCl/SO_4^{2-}
19.	Lakhi Shah Saddar III	-0.084	2.382	93.411	0.15	80.03	-2.32	1.63	0.62	NaCl/SO_4^{2-}
20.	Ghazi Shah	-0.18	0.758	85.014	0.12	53.25	-0.76	0.49	-	-
21.	Kai	0.53	0.938	92.817	0.08	61.86	-4.21	0.74	-	-
22.	Thoba	0.83	3.563	85.886	-1.00	77.12	-3.51	0.71	0.21	NaCl/HCO_3^-
23.	Khumb	0.28	3.586	90.471	-0.19	80.36	-4.82	0.78	0.15	NaCl/HCO_3^-
24.	Inchaile Sir	0.21	1.209	78.563	0.59	56.63	-5.15	0.63	0.34	NaCl/HCO_3^-

- = Not determined

Table 5. Descriptive statistics of springs of Sindh

Parameters	No. of samples	Minimum	Maximum	Mean	Standard error	Standard deviation
pH	24	6.60	8.10	7.44	0.07	0.36
EC	24	887	14160	3966	683	3346
Sal.	24	0.20	7.40	1.98	0.37	1.85
TDS	24	567	9062	2544	438	2146
T.Alk.	24	82	467	242	23	113
Hardness	24	126	767	406	39	195
Ca	24	34	315	126	16	81
Mg	24	18	177	63	8	39
Sulphate	20	112	969	226	48	235
Water °C	24	26	47	32	1.39	6.84
Na	24	51	1998	446	96	474
K	24	7	105	32	5	24
Cl	24	111	4266	825	203	996

(16.3%) indicated TDS within maximum permissible limit for drinking water (WHO, 2004, 1000mg/L). High concentration of alkalinity imparts bitter taste and makes water unpalatable (Monique, 2003). This was within the range 82-467mg/L with maximum for Abdullah Shah Ghazi and minimum at Kai spring. The chloride ions as sodium salt indicate salty taste when present in amount more than 250 mg/L in water. The chloride content in the springs were observed within 111-4266mg/L with maximum at lakhi shah saddar spring II and minimum at Kai spring. Three springs (12.5%) indicated chloride within WHO permissible limits for drinking water (WHO 2004, 250mg/L). In drinking water the sulphate concentration over 250mg/L causes cathartic action especially in children and tarnishes bad taste to water. The amount of sulphate was observed in range between 112-

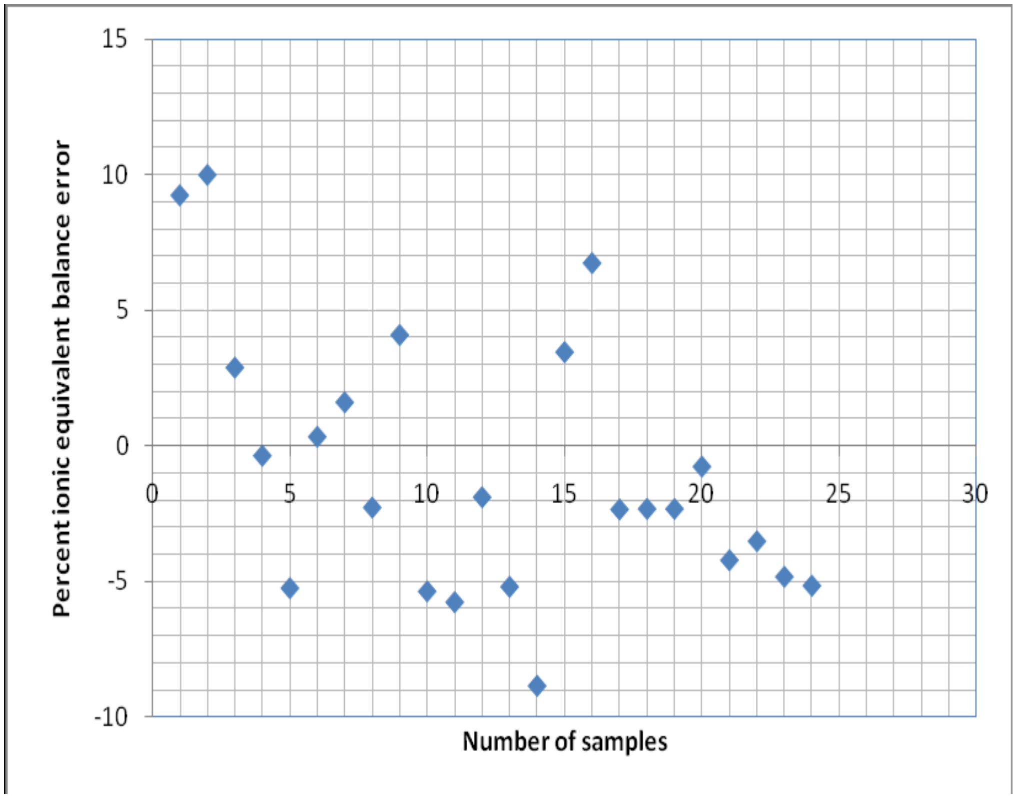

Fig. 8. Percent ionic equivalent balance error against springs

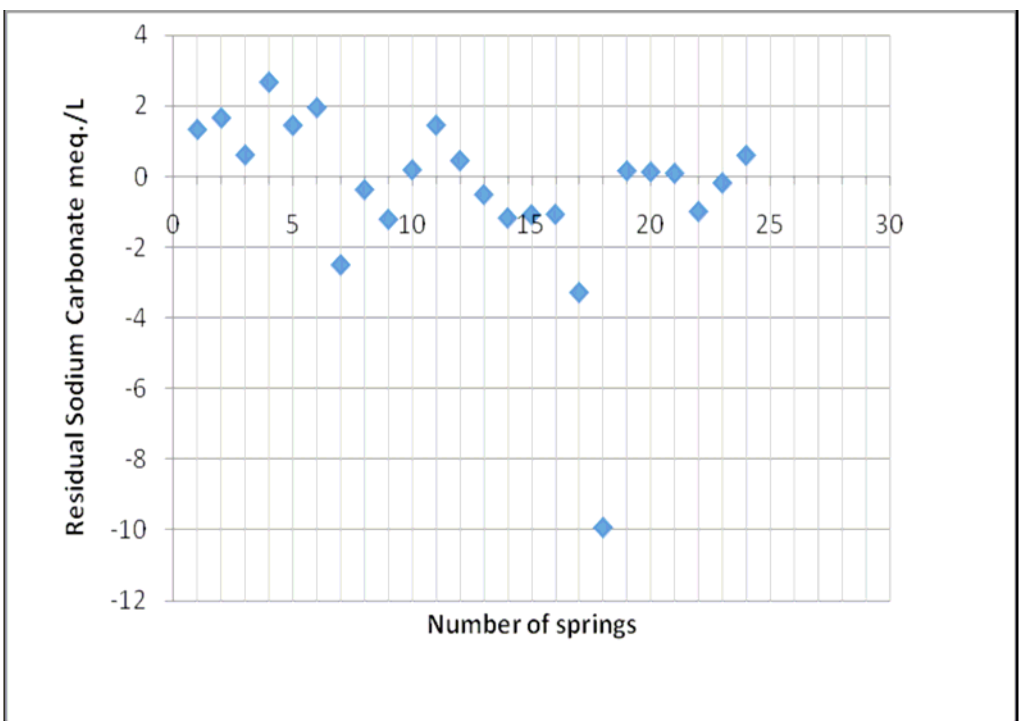

Fig. 9. Residual Sodium Carbonate against number of springs (values in milliequivalent/L)

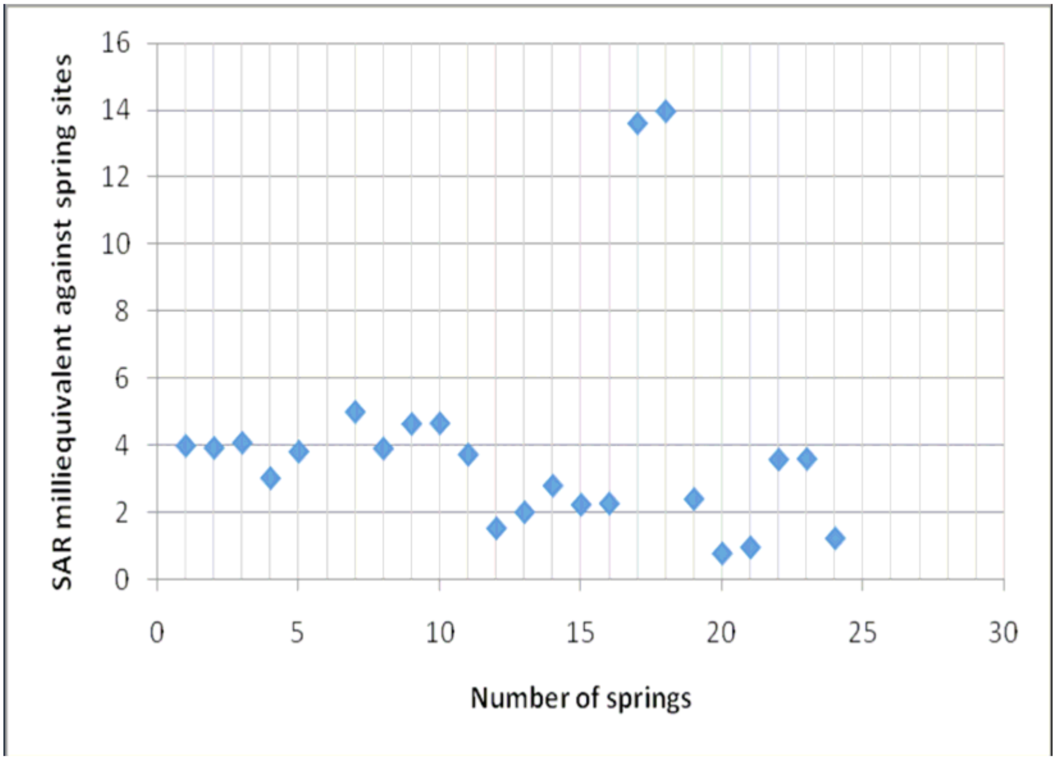

Fig. 10. SAR in milliequivalent against springs

Table 6. Factor analysis load of eigen values with cumulative percent of springs of Sindh

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	8.896	68.433	68.433	8.896	68.433	68.433	8.898	68.433	68.433
2	1.554	11.685	80.386	1.554	11.953	80.386	1.554	11.953	80.386
3	0.916	7.048	87.434						
4	0.634	4.875	92.309						
5	0.473	3.640	95.949						
6	0.327	2.512	98.461						
7	0.094	0.720	99.180						
8	0.058	0.449	99.629						
9	0.025	0.189	99.818						
10	0.017	0.134	99.951						
11	0.004	0.033	99.984						

969mg/L with maximum for lakhi shah saddar spring II and minimum for lal bagh. At the extent of seventy percent of springs indicated sulphate concentration within permissible limits of WHO for drinking water (250 mg/L). It have been reported in areas where drinking water contains greater than 500 mg/L as $CaCO_3$, there is higher incidence of gallbladder disease, urinary stones, arthritis and arthropathies Muza-levskaya *et al.* (1993); high concentration of calcium carbonate in water generates no lather and creates scaling problem in boilers (Monique, 2003). The hardness in the spring water was observed within 126-767mg/L, with maximum in Gharo I and minimum for lakhi shah saddar III springs respectively. Seventeen percent of the springs indicated hardness within permissible limits of WHO (200mg/L). Sodium, potassium, calcium and magnesium were determined in spring waters and the results obtained were in the range of 51-1998mg/L, 7-105mg/L, 34-315mg/L and 18-177mg/L respectively (Table 3). All the springs indicated a similar trends in the concentration of metal ions with the decreasing order Na>Ca>Mg>K, where the sodium was observed as dominant ion. A higher amount of Na intake may cause hypertension, congestive heart diseases and kidney problems (Singh *et al*., 2008). Its high content also decreases seed germination and agricultural productivity.

Table 7. Component Matrix, variable loadings on first two factors after varimax rotation

Parameters	Factor1	Factor 2
TDS	0.989	0.088
EC	0.989	0.088
Salinity	0.983	0.091
Na	0.966	0.149
Cl	0.966	0.092
Sulphate	0.942	0.185
Mg	0.942	-0.174
Ca	0.899	-0.330
K	0.742	0.093
pH	-0.732	0.080
Water ºC	0.300	0.815
Hardness	0.601	-0.666
T.Alkalinity	0.150	-0.451
Eigen value	8.896	1.554
% variance explained	68.43	11.95

A characteristic of potassium is similar to that of sodium and imparts salty taste. The important role in metabolic activity and maintaining osmotic pressure. Calcium and magnesium are essential elements, but their higher concentration converts the water to hard and may cause health problems Muza-levskaya *et al.* (1993). A significant concentration of Ca and Mg may develop sweet taste to the water. The concentration of Na, K, Ca, and Mg in the spring waters were compared with the permissible limits of WHO (2004) and was observed that 7 springs for Na, 14 springs for K, 5 springs for Ca and 4 springs for Mg indicated concentration levels within permissible limits of WHO.

Table 8. Correlation Matrix of springs in Sindh

Parameters	pH	EC	TDS	T.Alk.	Hard.	Ca	Mg	Sulphate	Water °C	Na	K	Cl
pH	1.000											
EC	-0.671	1.000										
TDS	-0.670	1.00	1.000									
T.Alkalinity	-0.159	0.144	0.145	1.000								
Hardness	-0.455	0.516	0.516	0.214	1.000							
Ca	-0.662	0.851	0.852	0.203	0.761	1.000						
Mg	-0.551	0.890	0.891	0.143	0.726	0.911	1.000					
Sulphate	-0.687	0.957	0.955	0.078	0.393	0.761	0.794	1.000				
Water °C	-0.158	0.354	0.356	-0.096	-0.267	0.006	0.171	0.366	1.000			
Na	-0.694	0.973	0.972	0.119	0.496	0.781	0.849	0.963	0.421	1.000		
K	-0.434	0.745	0.749	0.036	0.288	0.664	0.742	0.644	0.214	0.638	1.000	
Cl	-0.701	0.966	0.964	0.054	0.535	0.828	0.856	0.963	0.334	0.983	0.602	1.000

CONCLUSION

The analysis of 24 natural springs located within Karachi city, district of Thatta, Jamshoro and Tharparkar Sindh, Pakistan were examined for 15 different parameters. pH of all springs were within acceptable limits for drinking water. The EC and chloride of four springs were within desired limits of WHO for drinking water. Seven springs reported were observed as thermal springs with their temperatures above than the surroundings. The sulphate and hardness of fourteen springs were observed within maximum permissible limits for drinking water. The sodium, potassium, calcium and magnesium showed acceptable concentrations for drinking in 7, 14, 5 and 4 springs respectively. The highest concentrations were found among two of distant springs located at Lakhi Shah Saddar, district Jamshoro and Baba Bukhari Karsaz springs of Karachi region. Most of springs are highly important for tourism. Almost all springs are located near to holy shrines of saints. Some of springs are used for therapeutic purposes, for sufferer's of skin diseases. Separate bath rooms are used for men and women. A few of springs are used for cultivation purposes. Nearly one third of springs are suitable for drinking and could be used for bottle mineral water industry. Some of thermal springs exercised to generate electricity to meet with increased requirement. The extraction of sulphur and valued minerals could be utilized for economic development.

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