

Hydro-geochemistry of the Indus Basin in Rahim Yar Khan District, Central Pakistan

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Summary: Hydro-geochemistry of 135 water samples, collected at depths of 75 to 250 feet from tube wells in 1300 km² area, indicates that 1) the water is highly mineralized, with electric conductivity values > 22500 micromohs/ cm in over 75 % of the area, and 2) the mineralization increases from northeast to southwest. The amounts of total dissolved solids (TDS) and sodium adsorption ratio (SAR) range from 515 to 26650 and 3 to 54 mg/ l, respectively, but in > 85 % of the area the TDS values are >11000 and SAR values >30. In most of the samples, pH varies between 7.5 and 8.3 (overall range 6.9 to 9.2) and organic content between 50 and 100 mg/ l (overall range 20 to 185). The dissolved constituents (Na, Mg, Ca, K, Cl, SO₄, HCO₃, P and Cr) are dominated by Na (mostly 200-300 m eq/ l), Mg (variably high; 40-100 in 76 % analyses), Cl (mostly 123-316) and SO₄ (55-216 m eq/ l). Nearly 83 % of the analyses classify as sodium chloride type, and 17 % sodium sulfate type, with some Mg component in many. The data suggest that the groundwater belongs to a single, large aquifer. The concentration of dissolved solids and the salinity reflect the influence of geologic and hydrologic factors on the groundwater in the area. Much of the water is saline and seemingly associated with the highly soluble evaporite deposits occurring nearby. Only 10 % of the groundwater in the northeastern part of the area, occurring at shallow depth below 75 feet and probably diluted by seepage from canals and the Indus River, can be used for irrigation. Ninety percent of the groundwater shows hard type of incrustation.

Introduction

This paper deals with the hydro-geochemistry of 1300 km² area of Rahim Yar Khan (RYK) district in southern Punjab (70° 00' to 70° 45' E, 28° 00' to 28° 45' N). The area encompasses all the lands commanded by the Minchin, RYK and Sadiq Branch canals, their distributaries and minors (Fig. 1). It stretches for 65 x 20 km and slopes gently towards the south-west. The area has an arid climate characterized by high temperature (up to 49 °C), low rainfall, irregular humidity and, generally, high evaporation rates. May and June are the hottest months with a maximum mean temperature of 43 °C. January is the coldest month with a minimum mean temperature of 4 °C. Mean annual precipitation is 9 cm, of which 70 % occurs in the monsoon period of July and August.

The study area consists of a thickened sequence of unconsolidated flood plain deposits and aeolian deposits of Pleistocene to Present age. The former comprise both abandoned- and active flood plain deposits consisting mainly of loose to friable, well-packed, fine- to medium-grained sand, silt and

clay. Calcium carbonate concretions ("kankar") of irregular shape, but of regular size and distribution, are generally associated with these sediments. Data obtained from several wells of the area and surroundings show that the alluvium is more than 1500 feet¹ thick [1]. The alluvial complex, according to previous studies [2, 3], is of heterogeneous nature and shows limited vertical and horizontal extension of beds. The south-eastern part of the study area comprises aeolian deposits of the Cholistan desert. The sand plain consists of high sandy ridges and inter-dunal hollows, which are subrecent to older channels of Hakra River [4]. The aeolian deposits are the youngest in the area and commonly occur as active westward moving dunes 7 to 20 feet high. These deposits are composed of fine sand and silt with well-rounded and well-sorted grains. Most of this material is derived from the adjacent arid zone by wind action.

The aeolian deposits occur above the water table and have probably no hydrological significance, except at a few places where the zone of saturation

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¹Since the monitoring of groundwater levels by WAPDA is still carried out in feet, we have avoided using meters for the sake of conformity.

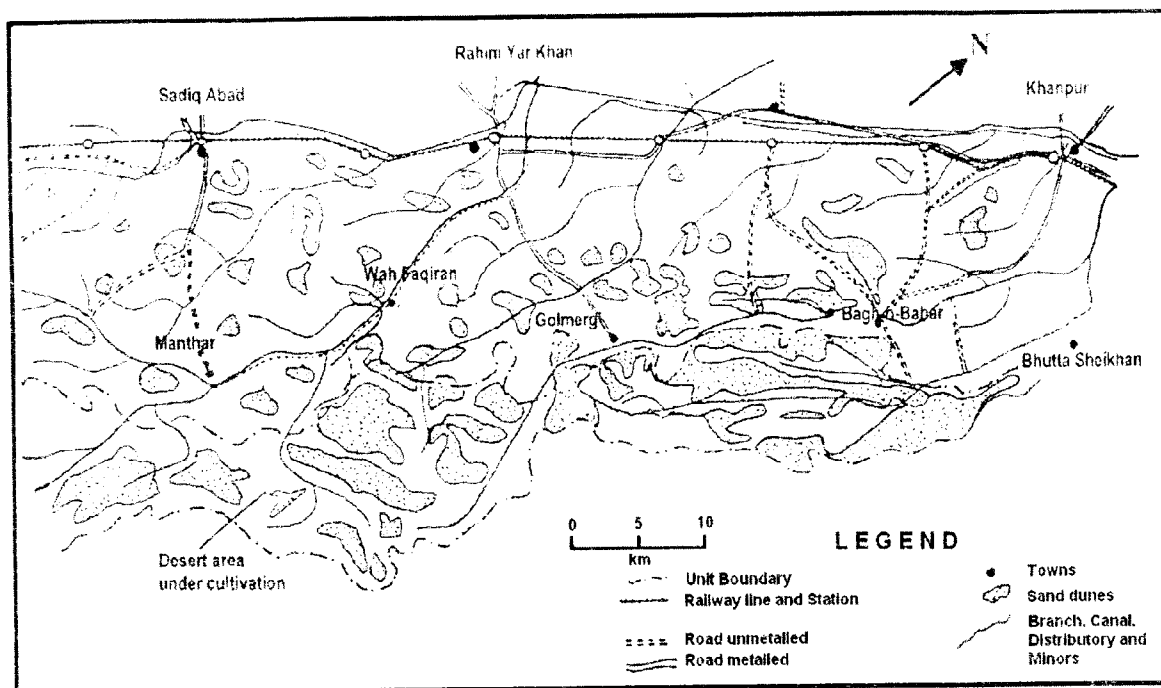


Fig. 1: Physiographic map of the Rahim Yar Khan area, southern Punjab (modified after Kamal and Shami, 1965).

may be within them. The sediments, formed as channel infills, levees and overbank flood plain deposits, show both lateral and vertical variation. This is due to the cyclic shifting in the course of the Indus River and its tributaries which laid down these sediments. The grain-size decreases laterally from northeast to southwest, which points to heterogeneous conditions of deposition, and a cause for variation in the permeability values of the layers. The absence of continuous clay layers, in general, is indicative of the presence of unconfined aquifers in the fluvial sediments. However, the presence of 5-15 feet thick clay lenses at some places suggests that semi-confined and confined conditions are present locally. In most of the area, depth to water table is between 6 and 8 feet. The coefficient of transmissivity in various parts of the aquifer (calculated both from equilibrium and non-equilibrium conditions from pumping tests, sieve analyses and specific capacities) and specific yield values range from 1592 to 2423 m^2/day and 4.16×10^{-3} to 1.6×10^{-3} , respectively [5]. The regional geologic factors that directly influence the permeability and transmissivity are lateral lithological changes, variation in sand thickness and grain-size distribution. In order to control the effects of groundwater exploitation, depths to water table should be frequently monitored in wells.

As in most parts of the world, groundwater is one of the principal sources of industrial, public and rural supplies in RYK district. In addition, on account of its good quality in shallow strata, groundwater is used for irrigation in the area. Broadly, groundwater in the region is divided into shallow and deep horizons on the basis of difference in origin and hydrologic history with respect to water quality. The shallow groundwater occurs up to about 75 feet from land surface. Modified by the seepage from canals and their distributaries during the past 50 to 60 years, by direct infiltration from rainfall, and by the Indus River, it is considered to be of good quality. Water in the alluvial aquifer or deep horizons below 75 feet is believed to be unaffected by irrigation water.

Various reports on regional scale have been published on groundwater quality in Bahawalpur and adjoining areas [1, 2, 6]. These were confined essentially to the study of total dissolved solids in shallow and deep groundwater. Ashraf and Chaudhry [7] studied the quality of groundwater in Bahawalpur area on regional scale. Hydro-geochemical studies have been carried out in the neighbouring Cholistan [8] and Thar areas [9, 10]. During the present work, 135 water samples from tubewells were collected at depths between 75 and 250 feet to study the deep

water of the RYK area. The main objective of this investigation is to examine the quality of water and its suitability for various purposes.

Table-1: Representative analytical data for water samples from RYK Area.

Tube Well	pH	EC μ S / cm at 25 °C	Org.Sub mg/ l	T.D.S mg/ l	S.A.R.
8	7.10	27100	183.97	17615	43.46
11	7.20	30050	174.49	19532	38.51
14	7.00	34600	29.71	22490	41.52
15	7.10	32000	22.76	20800	35.45
18	7.30	26200	38.00	17030	31.47
21	7.70	26300	155.52	17095	32.21
37	8.10	32400	88.50	21060	32.67
45	7.80	31100	25.29	20215	34.85
49	8.00	3150	8.85	2047	9.86
59	8.00	40000	92.30	26000	47.85
67	8.00	41100	76.50	26650	41.78
75	8.10	17300	82.82	11245	21.81
76	7.90	34500	71.00	22425	33.37
86	8.60	1270	57.53	825	9.88
95	8.10	14900	120.75	9685	39.02
97	7.90	36800	N.D	23920	53.94
100	2.80	33100	142.88	21515	47.69
116	8.20	18000	139.72	11700	45.25
118	8.10	23500	144.30	15275	26.20
156	8.10	10800	20.23	7020	41.28
161	7.90	31050	70.91	20182	38.69
173	8.20	20400	36.67	13260	30.14
177	8.70	14450	25.92	9392	40.50
178	9.10	7400	N.D	4810	24.91
180	9.10	1630	N.D	1059	6.57
181	8.80	1210	45.00	786	6.72
182	9.10	1250	N.D	812	14.72
187	7.60	23650	53.23	15372	29.73
191	7.90	26850	56.71	17452	28.87
200	4.70	16400	50.60	10660	22.26
208	8.30	13750	46.01	8937	38.59
210	7.90	10450	50.33	6792	31.08
217	9.20	5690	88.00	3698	16.67
226	8.00	31460	58.93	20449	31.71
230	8.20	793	70.11	515	8.27
231	8.30	1960	N.D	1274	3.26
233	8.00	30150	88.60	19597	39.88
236	7.90	31060	92.30	20189	36.58
241	8.00	24960	111.43	16224	27.95
246	8.30	27300	158.68	17745	31.72
248	8.00	39060	144.02	25389	33.26
251	8.00	32450	150.67	21092	27.97
255	8.00	28000	111.27	18200	27.77
261	8.40	28360	114.43	18434	4.12

Results and Discussion

The groundwater in RYK can be divided into two categories; one occurring at depth in aquifer prior to the inception of irrigation, and the other at shallow depths, assumed to be the result of seepage from Indus river and irrigation system. Analytical data of 135 water samples, collected at depths of 75 to 250 feet, indicate that the water is slightly to very

highly mineralized. The groundwater is mainly of sodium chloride type, however, water from some wells is of sodium sulfate type. Mineralization increases from northeast to southwest.

The principal chemical constituents of the groundwater are sodium, magnesium, chloride and sulfate ions. Regionally, sodium is the dominant cation followed by magnesium and calcium. Chloride is the most common anion, followed by sulfate. Combinations of these ions form two general chemical types of groundwater – sodium chloride and sodium sulfate. Only one water sample is magnesium sulfate type. According to [23] scheme (Fig. 7), the samples classify as alkaline, having affinity of sea water, but one sample falls in the "alkaline earth fresh water with more alkalis prevailing sulfatic" field. There is general chemical uniformity, suggesting that the groundwater belongs to a single large aquifer. Near the northern boundary of the area, occurrence of local zones of relatively fresh water at depth of 75 to 250 feet suggests some degree of dilution caused by river and canal seepage, and precipitation or direct infiltration by rainfall. These are also the important factors for groundwater recharge to a depth of few hundred feet, diluting and flushing out highly saline groundwater from the area.

The TDS and SAR values of the groundwater vary considerably and range from 515 to 26650 mg/l and 3.3 to 53.9, respectively. On this basis the approximate boundaries of favourable area for potential development of ground water supplies have been marked (Figs. 5 and 6). It is calculated that approximately 4.5 % of the area below 75 feet depth is underlain by groundwater that can be used as such for irrigation purposes, whereas 5.5 % may be used for irrigation after mixing with canal water in an appropriate ratio to make it fit for utilization. The rest of the area is saturated with highly saline water unsuitable for irrigation purposes.

The chemical composition of the majority of the samples is indicative of "Highly saline water", whereas a few samples fall a little away from the other projected points. The highly saline water appears to be marine or lacustrine in origin and associated with Pleistocene to Recent sedimentary deposits. The excessive presence of dissolved solids, such as Na, Cl and SO_4 , indicate that the groundwater in RYK could be associated with soluble natural evaporites, notably halite and sulfates. The compo-

sition of groundwater eventually approaches natural brines as the water moves through these halite-rich evaporite deposits occurring on the southeastern boundary of the area. Calcium, sodium, magnesium, chloride and HCO_3 constitute the bulk of cations and anions at the headwaters of the Indus River [27], and are derived from silicate and non-silicate sources, but in lowland tributaries and some Punjab rivers, (Na+K) and ($\text{SO}_4 + \text{Cl}$) predominate. Carbonates are abundant in the drainage basin of the Indus river, therefore, it has been suggested that much of the Ca+Mg is derived from the weathering of carbonates [28, 29]. The same conclusion has been derived for the Ganga-Brahmaputra river system [30]. Gypsum/anhydrite dissolution may also be an important source of calcium in the headwaters of the Indus main channel [28].

Water quality maps based on dissolved solids showing concentrations from 1000 to 22500 mg/l were prepared in the mid-sixties [1, 5]. The present study, however, indicates that with the passage of time the concentration of dissolved solids has increased. The deterioration of water quality (between 75 to 250 feet depth) is suggested to be the result of vertical intrusion (upcoming) of underlying saline water into the fresh water zone due to excessive pumping. Water from wells in RYK shows irregular pattern of distribution of dissolved solids and SAR values, which gives support to the idea of deterioration in water quality by upcoming.

More than 90 % of water samples from the wells in RYK indicate hard type of incrustation because of high chloride and sulfate ions. The samples having low electrical conductivity and less dissolved solids (less than 400 ppm bicarbonates) may cause soft type of incrustation. However, nearly all the water samples are alkaline with pH value greater than 7, and expected to be less corrosive. Water samples having less than 1500 micromhos/cm and less than 500 ppm of chloride concentration may result in high corrosion on iron and steel.

Experimental

Hydro-geochemistry

Physical and chemical parameters of the water samples were determined using different techniques. The physical parameters include pH and electrical conductivity (EC), whereas the chemical parameters include calcium (Ca), magnesium (Mg), sodium (Na),

potassium (K), chromium (Cr), chloride (Cl), bicarbonate (HCO_3), sulfate (SO_4) and total dissolved solids (TDS). The pH and EC were determined by using the pH Electrode Wissencha D-8120 meter and Bachofer 7410 meter, respectively.

Ca, Mg, Na, K and Cr were determined by using the Perkin Elmer 3300 Atomic Absorption spectrometer, equipped with HGA 600 graphite furnace and AS - 60 autosampler. The water samples were directly aspirated into the atomic absorption after its standardization for specific elements under the air-acetylene flame condition and the concentrations were obtained in ppm.

Chloride was determined by the "Mercuric Nitrate Method" by using digital titrator [11]. In this method, Diphenylcarbazone powder pillow was added to a known volume of water sample and titrated with mercuric nitrate until the pale yellow color changed to light pink (end point). Sulfate was determined by "Turbidimetric Method" of Rossum and Villuruz [12]. In this method salfa Ver 4 powder pillow was added to the known water sample and the turbidity was noted at wavelength of 450 nm by using Hach DR-2000 photometer. Bicarbonates were determined by the method of magnesium sulfate precipitation (Fanson, 1985). Phosphorous was analyzed by adding vanadate-molybdate reagent to known volume of water sample, the optical density determined at wavelength of 470 nm by using Pye Unicam UV/Visible spectrophotometer [12]. Total Dissolved Solid (TDS) in the water samples was determined by drying the known volume of water sample to a constant weight at 180 °C (Franson, 1985).

Ca, Mg, Na, HCO_3 , Cl, SO_4 , EC, pH and TDS were determined in all the samples; K in 89, P and organic matter in 68 and Cr in 59 samples. The representative analyses are presented in Tables 1-3. Full list of sample analyses can be obtained from the authors on request. Computerized programs, such as SURFER and GRAPHER, were used for drawing subsurface contours for the concentrations of the determined variables of the samples (Figs. 2-6). Locations of the tube wells, in addition to those shown in the figures, can be had from the authors.

Hydrogen Ion Concentration (pH)

The hydrogen ion activity is a principal variable of the groundwater system because of its

Table 2. Representative cation analyses in water samples from Rahim Yar Khan Area.

Tube Well	Na m eq/l	Na %	Mg m eq/l	Mg%	Ca m eq/l	Ca%	K m eq/l	K%	Cr m eq/l	Cr%	Cations m eq/l
6	270.51	64.37	98.17	23.36	47.06	11.20	4.35	1.04	N.D	N.D	420.09
8	222.96	80.87	33.41	12.12	19.25	6.98	ND	ND	0.08	0.03	275.70
10	138.25	85.01	16.44	10.11	6.35	3.90	1.56	0.96	0.03	0.02	162.63
18	197.98	70.90	52.38	18.76	26.73	9.57	2.03	0.73	0.04	0.01	279.16
40	263.32	68.24	82.23	21.31	39.90	10.34	N.D	N.D	0.40	0.10	385.85
49	21.60	67.63	5.92	18.53	3.70	11.58	0.72	2.25	N.D	N.D	31.94
59	360.32	75.36	80.18	16.77	33.37	6.98	4.28	0.89	N.D	N.D	478.15
71	270.00	77.59	50.88	14.62	24.26	6.97	2.83	0.81	N.D	N.D	347.97
75	120.00	65.71	39.29	21.52	21.20	11.61	2.13	1.17	N.D	N.D	182.62
76	242.93	69.28	68.83	19.63	37.30	10.64	1.51	0.43	0.08	0.02	350.65
86	14.13	76.83	2.75	14.95	1.37	7.45	0.10	0.54	0.04	0.22	18.39
88	33.67	91.97	--	4.37	1.11	3.03	0.23	0.63	N.D	N.D	35.01
90	195.31	75.99	42.56	16.56	16.97	6.60	2.12	0.83	0.06	0.02	257.02
97	352.76	79.94	56.54	12.81	28.90	6.55	3.06	0.69	N.D	N.D	441.26
98	188.64	87.30	16.20	7.64	9.21	4.26	1.70	0.79	0.02	0.03	215.77
116	160.19	85.89	16.20	8.69	8.93	4.79	1.16	0.62	0.03	0.02	186.51
135	286.08	70.38	81.21	19.98	36.33	8.94	2.75	0.68	0.11	0.03	406.48
151	240.49	63.06	108.45	28.43	29.75	7.80	2.70	0.71	N.D	N.D	381.39
156	96.19	88.89	8.73	8.07	2.11	1.95	1.16	1.07	0.02	0.02	108.21
161	274.72	73.10	64.76	17.23	36.20	9.63	N.D	N.D	0.18	0.05	375.86
173	167.58	72.12	42.14	18.13	19.63	8.45	N.D	N.D	--	0.03	229.38
180	14.53	59.16	6.76	27.52	3.00	12.21	0.20	0.81	0.07	0.30	24.56
181	11.84	62.55	4.91	25.94	2.10	11.09	N.D	N.D	0.08	0.42	18.92
187	172.45	71.30	48.92	20.23	18.47	7.64	2.02	0.83	0.09	0.04	241.95
188	185.87	66.25	59.10	21.06	35.61	12.69	N.D	N.D	N.D	N.D	280.58
215	135.60	85.76	11.04	6.98	9.44	5.97	2.01	1.27	0.02	0.01	158.11
230	9.60	75.71	1.68	13.25	1.03	8.12	0.32	2.52	0.05	0.39	12.68
231	8.00	40.00	9.90	49.50	2.10	10.50	N.D	N.D	N.D	N.D	20.00
235	180.16	66.15	59.57	21.87	30.20	11.09	2.28	0.84	0.14	0.05	272.35
246	221.76	70.98	50.84	17.89	30.00	10.55	1.96	0.69	0.04	0.01	284.25
252	211.14	67.02	67.84	21.53	33.27	10.56	2.67	0.85	0.11	0.03	315.03
261	199.72	58.72	95.60	28.11	41.70	12.26	3.06	0.90	0.06	0.02	340.14

participation in most of the chemical reactions that affect the composition of water. Ignoring three abnormally low and possibly erroneous values (2.8 to 4.7), the pH in the analyzed samples ranges from 6.9 to 9.2, with more than 80 % being in the range of 7.5 to 8.3 (Table-1). The pH values tend to decrease from the northeast (NE) to southwest (SW) direction (Fig. 2). The tube wells RYK 177, 178, 180, 181, and 182 show higher pH values of 8.7 to 9.1, and much greater amounts of carbonates and bicarbonates than other water samples in the area. A positive correlation in the concentration of HCO_3^- and pH content suggests that the increase in the pH values may be related to the presence of bicarbonates and carbonates not only near these wells, but also in the entire area. Other causes proposed for the rise of pH in the groundwater [13] do not appear to be important as far as the area under study is concerned.

Specific Electrical Conductance (EC)

Electrical conductivity indicates the ionized salt contents of groundwater. Contour lines of 2000

micromhos per centimeter ($\mu\text{S}/\text{cm}$) concentration of conductance values have been shown in Fig. 3. The measured values vary between 793 $\mu\text{S}/\text{cm}$ and 41100 $\mu\text{S}/\text{cm}$ (Table-1), with a high concentration of 22500 + in 77 % of the area. The EC values increase from NE to SW and show a negative correlation with pH values. However, there is also a general decrease in EC towards the river. Local decrease, found in some places, may be related to dilution effect of the canals/distributaries or to infiltration by rain water. The high specific conductance, *i.e.* more than 10,000 to 40,000 $\mu\text{S}/\text{cm}$ in the individual water samples, is due to higher concentration of sodium, chloride, and sulfate ions.

Organic Substances

The close relationship between water in the hydrologic cycle and the living matter and its waste products ensures that all natural waters contain organic material. Soil, unsaturated zone and aquifer contain organic substances. The total concentration of organic material in water sample includes measure-

Table 3. Representative anion analyses in water samples of Rahim Yar Khan area.

Tube Well	CO ₃ m eq/l	HCO ₃ m eq/l	HCO ₃ %	Cl m eq/l	Cl%	SO ₄ m eq/l	SO ₄ %	PO ₄ m eq/l	PO ₄ %	Anions m eq/l
18	0.00	5.00	1.82	172.50	62.73	97.50	35.45	N.D	N.D	275.00
49	0.00	3.00	9.68	11.25	36.29	16.67	53.77	0.08	0.27	31.00
59	0.00	6.00	1.26	279.75	58.63	191.25	40.00	0.10	0.02	477.10
79	0.00	7.00	2.59	234.00	86.54	29.25	10.82	0.13	0.05	270.38
81	0.00	1.90	0.48	292.00	73.20	105.00	26.32	N.D	N.D	398.90
86	0.60	4.40	21.56	15.00	73.49	-	1.47	0.11	0.54	20.11
88	0.50	6.40	18.18	23.25	66.03	5.66	16.07	N.D	N.D	35.81
100	0.00	0.50	-	232.50	64.84	125.58	35.02	N.D	N.D	358.58
125	0.00	2.90	0.65	316.00	70.92	126.70	28.43	N.D	N.D	445.60
177	0.70	5.99	3.98	78.75	52.27	65.18	43.26	0.05	0.03	150.67
178	1.10	11.00	11.24	31.50	32.20	55.23	56.45	N.D	N.D	98.83
180	1.10	8.99	37.98	12.11	51.16	1.47	6.21	N.D	N.D	23.67
181	0.80	6.99	40.19	7.50	43.13	2.05	11.79	0.05	0.32	17.39
182	1.10	7.00	30.86	14.01	61.77	0.57	2.51	N.D	N.D	22.68
186	0.00	2.50	0.67	153.75	41.26	216.60	58.13	N.D	N.D	372.85
195	0.00	6.00	8.80	28.40	41.64	34.80	51.03	N.D	N.D	69.20
200	0.00	3.00	1.45	78.75	38.01	125.43	60.54	0.02	0.03	207.20
203	0.00	5.30	1.29	292.00	70.82	115.00	27.89	N.D	N.D	412.30
204	0.00	5.00	1.50	176.25	52.77	152.70	45.72	0.04	0.01	333.99
206	0.00	2.50	0.70	180.00	50.45	174.30	48.85	N.D	N.D	356.80
208	0.30	2.80	1.46	60.00	31.27	128.70	67.07	0.08	0.04	191.88
210	0.00	4.00	2.20	41.25	22.78	135.60	74.90	0.21	0.12	181.06
212	0.30	7.35	6.65	42.00	37.99	60.90	55.09	N.D	N.D	110.55
213	0.60	4.40	6.90	20.00	31.37	38.60	60.54	0.16	0.25	63.76
215	0.60	4.40	2.83	60.00	38.60	90.30	58.09	0.14	0.09	155.44
217	1.20	10.80	14.63	45.00	60.96	16.70	22.62	0.12	0.60	73.82
230	0.00	-	2.66	7.50	62.29	4.10	34.05	0.12	1.00	11.72
231	0.40	3.80	19.10	6.50	32.66	9.20	46.23	N.D	N.D	19.90
233	0.00	2.50	0.80	187.50	59.67	123.94	39.44	0.30	0.90	314.24
241	0.00	4.00	1.58	153.75	60.59	95.92	37.80	0.09	0.04	253.76
261	0.42	4.10	1.22	169.50	50.26	163.11	48.37	0.08	0.02	337.21

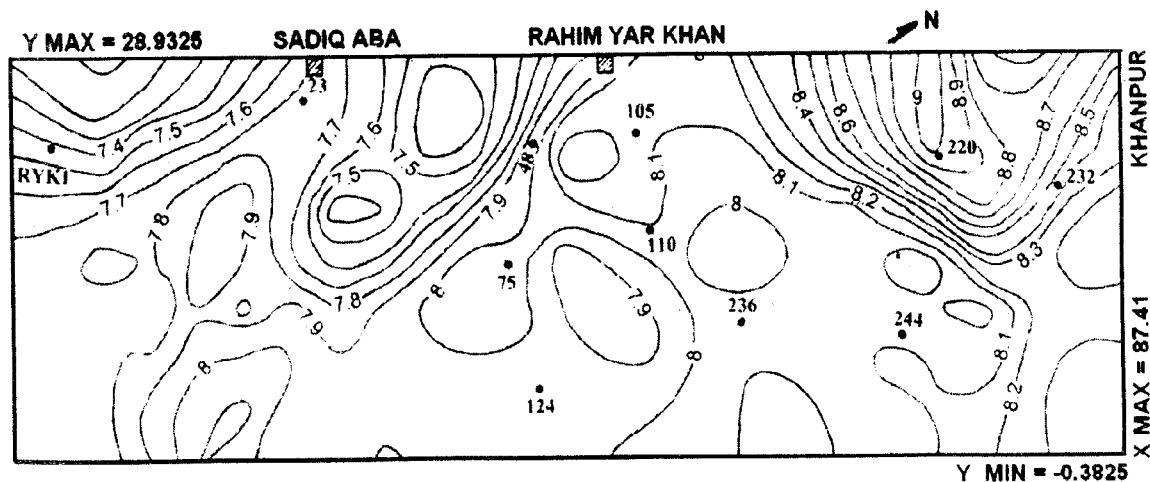


Fig. 2: Contours of hydrogen ion (pH) concentration for water samples of depth range of 75 to 250 feet in 1989. Contour interval is 0.1. Dots are for some tube well locations, numbered RYK 1...244.

ments of carbon contents, such as dissolved organic carbon (DOC) and total organic carbon (TOC).

Most of the analyzed groundwater samples in the study area show rather high concentration of

organic substances. In general, the total organic matter content of the water samples varies between 20 and 158 (mostly 50 to 100) mg/l. Some water samples, such as those from wells RYK 8 and 11, show even higher concentration, 184 and 174 mg/l,

respectively. The spacial distribution of the organic substances for the depth range of 75 to 250 feet shows no systematic trend in the area (Fig. 4). Normally, the concentration of organic carbon is higher in the surface water than in the groundwater. Excessive use of pesticides pollutants such as DDT, chloredane or other halogenated organic compounds might have affected the concentration of organic carbon, thereby rendering the water unsuitable for human use and aquatic life.

Total Dissolved Solids (TDS)

The areal distribution of TDS in the upper 75 to 250 feet of alluvial aquifer is shown through isogram contours (Fig. 5). The regional distribution of TDS corresponds to the electric conductance values (see Fig. 3). In conformity with the movement of water from NE to SW direction, the dissolved solids show an increase with increase of distance from NE to SW. The maximum TDS concentration detected in water from the alluvial aquifer is 26650 mg/ l (Table-1). About 85 % of the RYK area is apparently underlain by highly mineralized groundwater having TDS in the range of 11000 to 26650 mg/ l, while the remaining 15 % shows moderately low concentration of dissolved solids (2210 to 10660 mg/ l), with a very small portion having lower concentrations (515 to 2210 mg/ l). The favourable parts of the area for potential development of groundwater supplies can be assessed on the basis of the present geochemical investigation. The isogram of 1000 mg/ l demarcates an area with potential for development as an additional source for irrigation supply (Fig. 5). However, since the present data set is based on over 15 years old sampling, additional analyses of freshly collected samples may be required for verification.

Sodium Adsorption Ratio (SAR)

The SAR value is a measure of the concentration of Na to Ca + Mg. The SAR contents of the groundwater in RYK range from 3.26 to 53.94 mg/ l and show a gradual increase from the NE to SW (Fig. 6). About 80 % of the area is underlain by water with SAR values of over 30 (Table-1). Based on SAR parameter, 90% of the samples can be categorized as poor for irrigation purposes, with 3.7 % being fair, 2.2 % good, and 4.0 % excellent [14]. The TDS and SAR isograms (Figs. 5 and 6) show a degree of similarity. The area near the NE boundary is underlain by groundwater having TDS < 2000 ppm

and corresponds roughly with the area having SAR values < 12.

Cations

Sodium

Sodium is the major element present at depths ranging from 75 to 250 feet in the study area. It makes some 65 % to 82 % of the total cations. In 58 % of the analyzed samples the concentration of sodium ion ranges from 200 to 300 m eq/ l (Table-2). Of the rest, 37 % contain less than 200 m eq/ l Na. The remaining 5 % samples show Na concentration in excess of 300 m eq/ l. The high Na contents of the deep aquifer may be due to the presence of less permeable strata, such as clay layers [15, 16] found interbedded with fine sand in most of the boreholes in the area. Being less permeable for leaching and flushing by fresh water circulation, and for their high cation exchange capacities, clay minerals can retain Na for longer time. Obviously, use of such highly saline water would have injurious effect on the soil.

Magnesium

There is a high concentration of magnesium, exceeding 16 % in 65 % of the analyses. Its amount displays an overall range of 6.9 to 28.4 %, ignoring one lower and one higher value. The m eq/ l content exceeds 10 in most cases, being 50-100 in 76 % of the analyses (Table-2). The cation-exchange behavior of magnesium is similar to that of calcium. Both ions are strongly adsorbed by clay minerals and other surfaces having exchange sites. But magnesium has a very long residence time compared with calcium which would produce Mg: Ca ratio of above 1.0 and a high pH [17]. Due to the reduction of SO₄, CO₂ would be replenished and a high Mg concentration may ultimately be reached. No regional trend has been recognized and rather uniform distribution of magnesium ion has been found throughout the area.

Calcium

Like Mg, Ca is an essential element of plant and animal life and a major component of all natural waters. In most of the study area, the concentration of calcium ion varies between 3 and 11 % of total cations in the groundwater (Table-2). However, analytical data suggest the presence of local and small pockets with lower calcium concentration (1.0 to 10.0 m eq/l). The high concentration of sodium in the area, coupled with an inverse correlation in the

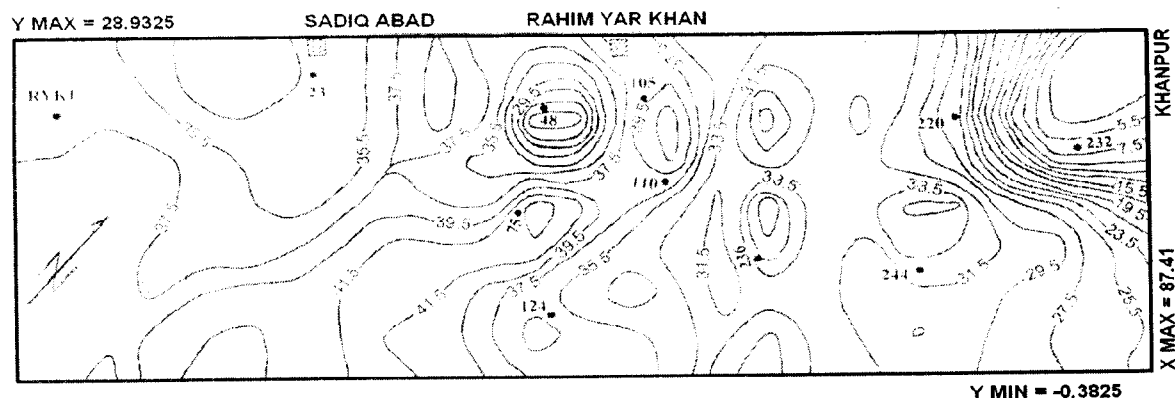


Fig. 6: Contours for sodium adsorption ratio (SAR) values at interval of 2. Other details as in Fig. 2.

amounts of Na and Ca, may be due to the exchange of these two elements [18].

Potassium

In most of the analyzed water samples the potassium concentration ranges from 1 to 3 m eq/ l, but in a few it is up to 4.35 m eq/ l (Table-2). Eight samples represent lower K concentration below 1.0 m eq/ l. Since the potassium ion is substantially larger than the sodium ion, it would normally be less readily adsorbed than sodium in ion-exchange reaction. This, along with its lower geochemical mobility than Na, may explain the concentration of K being lower than those of the other cations.

Anions

Chloride

Mineralization in the study area appears to be caused predominantly by chloride. The quantity of the chloride ion varies generally between 50 and 72 % of total anions; eight samples have higher and 22 lower amounts than these limits. The chloride content of 108 groundwater samples in the area is between 123 and 316 m eq/ l; 22 samples have less than 98 m eq/ l (Table-3). Four small pockets of low concentration were recognized in the area. These are situated between the wells RYK 86, 88 (pocket 1), RYK 178, 180, 181, 182 and 195 (pocket 2), RYK 208, 210, 212, 213, 215, and 217 (pocket 3), and RYK 230, 231 (pocket 4). The ranges of concentration of chloride in these pockets are 15.0 to 23.25 m eq/ l (pocket 1), 7.50 to 31.50 m eq/ l (pocket 2), 20.0 to 60.0 m eq/ l (pocket 3), and 6.50 to 7.50 m eq/ l (pocket 4). The

high Na and Cl in the area may be related to the presence of brine.

Sulfate

Sulfate, the second dominant anion in the study area, ranges from 216 to 55 m eq/l in 120 samples; the remainder having lower amounts. Concentration less than 16.0 m eq/ l were detected from the samples taken from water wells RYK 49, 86, 88, 180, 181, 182, 217, 230, and 231 (Table-3). The principal geologic source of sulfate may include materials present in the sedimentary rocks that were oxidized during weathering. Evaporite deposits may contain a range of sulfate minerals and some carbonaceous concretions (kanker deposits) can also be a source of sulfate. It can also be derived from gypsum/anhydrite through total substitution of Ca by Na. But the high SO_4 , Cl, Mg, and Na in the analyses of the water samples suggests their derivation from evaporite minerals such as halite (NaCl) and, possibly, mirabilite ($\text{Na}_2 \text{SO}_4 \cdot 10\text{H}_2\text{O}$) and kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$).

As the study area has low rainfall, accumulated solutes are reclaimed by irrigation. Since the introduction of weir-controlled irrigation in 1932, followed by the supplementing irrigation supplies in 1960's, the increased water supply may have leached away the solutes in the drainage water or return flow. Such a process will increase the concentration of dissolved solids and loads in the residual water of the affected area [19, 20]. Evapotranspiration also contributes to increase the sulfate concentration. Another factor which may cause the

increase of sulfate content is the presence of insufficient concentration of calcium to maintain a gypsum solubility control [18].

Bicarbonates

Most analyzed samples (130) show concentration of bicarbonates (HCO_3) between 1.45 and 9.0 m eq/l (Table-3). Four higher values range from 10.6 to 15.6; one abnormally low value (0.32) may be erroneous. Water samples taken from wells RYK 100 and 230 have a concentration of 0.32 and 0.50 m eq/l. Bicarbonate concentration in the water has increased in some wells, whereas in others it has decreased. From a vague positive correlation between pH values and HCO_3 concentration as well as percentage, one would expect that HCO_3 would increase from northeast to southwest. However, the change in concentration takes place in such a short distance that it is not possible to infer regional trends.

Phosphorous and Chromium

Phosphorous is essential for plant and animal nutrition. The analyzed samples have phosphorous contents from 0.04 to 0.21 m eq/l (Table-3), with one value of 0.3 and two of 0.02. The northeastern part of the area has higher concentration of phosphorous than the central and southwestern part. Most of the groundwater samples in the area show concentration of chromium from 0.02 to 0.09 mg/l, but samples from wells RYK 135, 140, 164, 235, 242 and 252 show higher concentration (0.10 and 0.11 mg/l). The samples from the wells RYK 161 and 40 have abnormally high (erroneous?) concentrations of 0.18 and 0.40 mg/l (Table-2). It appears that the Cr content in the groundwater is related to the waste disposal [21].

Graphic Presentation and Classification

Stiff's Pattern Diagram

The hydro-geochemical data of 135 tubewells have been processed according to Stiff [22] and used in the evaluation of the types of salts existing in the groundwater. The method is based on plotting cations and anions on XY axes. This classification is useful to study the future trends of change in groundwater as pumping continues. It is also helpful to a certain extent in assessing corrosive and incrustating capabilities of groundwater. The water samples from RYK are dominated by Na amongst the cations and chloride amongst the anions, and can be classified

into two major categories: 1) Sodium Chloride: 83.6 % of the 135 samples, and 2) Sodium Sulfate: 16.3 % of the 135 samples. In one sample, Magnesium Sulfate type is dominant.

Piper's Diagram

The analyzed samples contain 61 to 93 % alkalis (dominantly sodium), 58 to 100% sulfate and chloride, with less than 40 % bicarbonate in a few. A comparison with the map of EC values (Fig. 3) indicates that the area for this type of groundwater is corresponding with the region of the highest EC-values. Hydro-geochemical data of the groundwater samples have been plotted on classification diagram for anion and cation facies (Fig. 7) developed by Piper [23]. On the basis of cations ternary diagram (Ca—Mg—Na+K), the water classifies as sodium type. On anion ($\text{Cl—SO}_4\text{—CO}_3\text{+HCO}_3$) basis, most samples classify chloride type, but some sulfate type. Projections of the analyses on the quadrilateral are concentrated along the $\text{SO}_4\text{+Cl}$ edge, barring those of tube wells RYK86, 88, 178, 180, 181, 182, 217, 230, and 231. All but three analyses plot in NaCl field; two in NaHCO_3Cl field and one in CaNaCl field. Several analyses have substantial Mg/ NaSO_4 component (for further details of the diagrams, see [23 - 25]). It can be concluded that 1) the analyses are dominated by alkalis, 2) they classify as NaCl type, and fall in the area typical of seawater and oil/gas fields waters, and 3) their clustering is suggestive of a single, isolated aquifer.

Hydrogeochemical Facies

The chemical composition of the water samples of most wells is suggestive of their highly saline nature. Although it has been suggested that groundwater tends to evolve chemically toward the composition of seawater [25], the highly saline nature of the groundwater in RYK is probably of lacustrine or marine connection. The presence of highly dissolved solids, such as sodium, chloride, and sulfate, indicates that the groundwater composition in RYK has modified as a consequence of association with evaporites of highly soluble nature related to the Pleistocene—Early Recent deposits. Presence of evaporite deposits on the south of RYK lends support to the idea that the saline water is related to lacustrine/marine environment. Water moving through evaporites eventually becomes saturated with respect to the solutes and acquires a composition like natural brines. The equilibrium conditions for sodium

3. The analyzed samples of water are alkaline (pH > 7), and expected to result in usually low corrosion.

4. The specific electric conductivity of more than 95 % water samples is greater than 1500 $\mu\text{S} / \text{cm}$, which may cause corrosion of iron and steel.

5. Chloride concentration of 500 ppm in 95 % of the samples is indicative of some corrosive character.

Conclusions

1. Groundwater mineralization in the 75 to 250 feet depth zone, based on 1989-90 data, increases from northeast to southwest in the Rahim Yar Khan area.
2. The groundwater in 83 % of the area is sodium chloride type and in 17 % area sodium sulfate type.
3. Much of the groundwater is highly saline and the salinity appears to be related to evaporite deposits of lacustrine or marine origin.
4. Deterioration of the groundwater quality is due to a) leaching from local evaporite deposits, and b) upcoming of underlying saline water into freshwater as a consequence of excessive pumping.
5. Hard type incrustation can be caused by 90 % of the wells water. Most samples are mildly alkaline to neutral, indicating usually less corrosive nature.
6. Most of the groundwater is highly mineralized and not good for irrigation. In order to avoid enrichment of dissolved ions in the upper 75 feet, irrigation from deeper groundwater should be reduced.
7. Groundwater in only 4.5 % of the area (with EC < 3000 microohms/ cm) is usable for irrigation. Another 5.5 % is usable for irrigation after mixing with canal water.
8. With the exception of two wells, the EC values, and amounts of chloride, sulfate and sodium, render the water unsuitable for drinking.

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