CHARACTERIZATION OF WATERS

Part I. Spring Waters in and Around Karachi.

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The quality of water from 16 springs located within 150 km radius of Karachi has been evaluated. The paper describes in detail the various physical and chemical characteristics. An attempt has been made to assign possible reasons for the variation in their chemical composition and to classify them according to their quality.

INTRODUCTION

Precipitation on land feeds the rivers and lakes and percolation of surface run-off builds up the underground potential. Ground waters form only about 0.6% of the total volume of water in the hydrosphere, while the terrestrial surface water constitutes less than 0.02%[1,2]. In cases where the percolated water collects on an impervious bed of rock it is forced back to the surface as spring water by the pressure of the supper incumbent layers. Spring waters are classified as ground water although the latter is usually considered synonymous with well water. Bryan[3] has classified the springs into two types: (i) those resulting from non-gravitational forces e.g. volcanic springs, associated with volcanic rocks, fissure springs or thermal springs, resulting from fractures in the earth's crust, (ii) those resulting from gravitational forces which is the case obtained for water flowing under hydrostatic pressure e.g. depression springs, contact springs, artesian springs and tubular or fracture springs. Generally the classification of spring waters is made either on the basis of their chemical composition or on geological conditions governing the point of their location. They have, for example, been classifed as alkaline, acidulous, bitter, chalybeate or ferruginous, hepatic, siliceous, iodine etc.

Spring waters are of potential value and there are a number of springs in and around Karachi. Table 1 lists their name, location and capacity. In spite of the fact that Karachi is faced with water scarcity problems due to rapid increase in population and industrial activity, very few studies, if any, have so far been undertaken either for their scientific evaluation or for exploitation, although it is well known that spring waters have certain advantages over other water supplies e.g. they are naturally clear, contain fewer bacteria, have a more constant temperature and also have a uniform mineral content. The present study describes the chemical composition of 16 spring waters around Karachi and attempts to classify them according to their quality.

METHODOLOGY

Most of the samples were provided to these Laboratories by Geological Survey of Pakistan for which the authors are thankful to Mr. Farhat Husain, Director. The remaining, particularly those in the immediate neighbourhood of Karachi were collected by these Laboratories.

Physical measurements and chemical analysis were carried out by standard methods[4,5]. Detailed chemical analyses of the samples are shown in Table 2.

RESULTS

Physical Properties. Almost all the samples of spring waters when received were colourless and had no significant turbidity, suspended solids or settleable solids. Seven out of the 16 samples viz. 6, 10, 11, 12, 14, 15 and 16 had sweet taste, while samples No. 1, 3, 4, 7, 9 and 13 were slightly saline and No. 2, 5, and 8 were highly saline. Temperature recorded at the source indicates that all except 5 and 7 are cold springs.

pH. The spring waters have been found to have pH value as shown in Table 2 ranging between 7.75 and 8.75 indicating that they are weakly alkaline. Only two samples viz. No. 2 and 15 have pH lower than 8.0 while all others have values in the higher range.

Electrical Conductivity. Conductivity measurements show that sample No 2 had the highest conductivity i.e.,

1.502 mmhos/cm while No. 10 has the lowest i.e. 1.09 mmhos/cm. This may apparently be due to the correspondingly high and low total dissolved solids content in the samples. It may be noted from Table that all sweet water springs have a conductivity lower than 2.186 mmhos/cm. It has also been observed that after boiling and reducing a 250 ml aliquot to 200 ml, the conductivity of samples from sweet water springs No. 6, 10, 11, 12, 14, 15 and 16 virtually decreases, while there is considerable increase in conductivity after boiling in the remaining samples.

Chemical Properties. Alkalinity: Total alkalinity of the samples has been found to be in the range of 150-440 ppm estimated as $CaCO_3$. The highest total alkalinity 440 mg/lit. is noted for sample No. 1 and the lowest 150 mg/lit. is for sample No. 11.

Phenolphthalein alkalinity (P) ranges between 0-60 ppm. Seven samples have P-alkalinity, six having not more than 20 ppm while sample No. 1 has a value of 60 ppm. None of the sweet water samples have significant P-alkalinity excepting No. 16.

Methyl orange alkalinity (M) lies in the range of 140-420 ppm. M-alkalinity is present in all the samples and total alkalinity(T) is found greater than 2P which indicates the absence of caustic alkalinity. The alkalinity is mainly due to bicarbonates of calcium and magnesium. Carbonates are present in some samples but are quite low in concentration.

Total Dissolved Solids (TDS): The amount of total dissolved solids has been found in the range of 610 to 8,165 ppm. The lowest TDS, 610 ppm is found in sample No. 10 which has sweet taste and the highest 6,165 ppm is for sample No. 2 which is highly saline. Samples No. 6, 10, 14, 15 and 16 having sweet taste have a TDS below 1,000 ppm while samples No. 11 and 12, though slightly brackish, have a TDS below 1,000 ppm, the remaining have a value more than 1,000 ppm.

Chlorides: The chloride content of the samples ranges between 99.0 and 3,446 ppm. Samples No. 2,5 8 and 9 have a high chloride content ranging between 765 and 3,446 ppm, with No. 2 having 3,446 and 13 have a chloride content higher than 300 ppm but less than 450 ppm, while No. 1, 6, 10, 11, 12, 14, 15 and 16 do not have more than 250 ppm.

Eight samples viz. No. 3, 4, 5, 7, 8, 9 and 11 have chlorides higher than the other anions i.e. sulphate, bicarbonate etc. while the remaining have it less than the bicarbonates.

Sulphates: Sulphate concentration of the samples ranges between 41 and 1,560. The highest value of 1,560 ppm is noted for No. 2 which also has the highest TDS and chlorides. Samples No. 2 and 5 have a value higher than 1,000 ppm. The sulphate content is less than 250 ppm in all excepting No. 8. The sulphate concentration in 12 samples is less than the amount of chloride and bicarbonate and only in four viz. 2, 5, 8 and 11 it is higher than bicarbonates but lower than chlorides.

Bicarbonates and Carbonates: Carbonate content has been found to be almost negligible in all the spring water samples. Bicarbonates are present in each sample and its concentration ranges between 127 and 410 ppm. The highest value of 410 ppm being in sample No. 9 and the lowest 127 in No. 11.

Chloride and not bicrbonate concentration seem to be deterministic of taste e.g. sample No. 2 which is highly saline has a bicarbonate concentration of 332 ppm while No. 14 having the same bicarbonate concentration as the former is sweet tasting. All excepting No. 11 have bicarbonate content more than 200 ppm.

All sweet water samples have been found to have bicarbonate content significantly higher than chloride and sulphate, while the same is lower than chlorides and sulphates in those which are highly saline.

Calcium: Calcium content of the spring water samples ranges between 30 and 449 ppm, the highest (449 ppm) being in No. 2 and the lowest (30 ppm) in No. 1. Highly saline samples No. 2, 5 and 8 carry a relatively high calcium concentration than those having sweet water.

Magnesium: Magnesium ion content of the spring water samples ranges between 32 and 457, the highest (457 ppm) being in No. 2 while the minimum (32 ppm) is in No. 15. Magnesium content like calcium is high in highly saline springs and the variation pattern in other springs is similar to that of Ca^{++}.

Sodium: The sodium ion concentration of the samples closely follows the variation pattern of TDS and chloride content. The maximum Na^+ concentration (1,725 ppm) is found for No. 2 which is a highly saline spring and the minimum (80 ppm) is for springs No. 10 and 14 which have sweet taste. Only No. 15 has a sodium ion content slightly lower than Ca^{++}, in all the others it is higher than any other cation viz. Ca^{++}, Mg^{++}, K^+ etc.

Potassium: Potassium ion is present in relatively small quantity in the samples under study, it ranges between 3 and 32 ppm with saline spring water samples having it lower than 20 ppm. The variation pattern is similar to that of sodium. In the descending order for the amount of anions and cations, K^+ content is always the lowest.

DISCUSSION

Soluble salts found in ground water originate primarily from rock materials[7]. The areas, where the springs under

Table 1.

Sl. No.	Name	Location	Discharge/Capacity
1.	Abdullah Shah Ghazi spring	Near tomb of Abdullah Shah Ghazi, Clifton, 10 km south of Karachi.	The water at the source is arrested in the form of a small pond and discharge balances the amount withdrawn.
2.	Goth Bhawani Sarai spring	3 miles north of goth Bhawani Sarai on RCD highway, 6.5 km east of Hub Chowki	Temporary spring, remains constant in a small tank; the discharge balances the amount withdrawn.
3.	Dhabejee spring No. 1.	50 km west of Thatta, near Dhabejje Railway Station	The discharge rate is 0.18 cusec
4.	Dhabejee spring No. 2	1 km from spring No. 1	The discharge rate is 1.2 cusec
5.	Karsaz spring	Near Karasaz, 10 km east of Karachi on Share Faisal at tomb of Pir Bukhari	The water at the source is arrested in the form of small tank and the discharge balances the amount withdrawn.
6.	Khadeji spring	About 65 km north-east of Karachi and 5 km north of Super Highway	The discharge rate is about 9.0 cusecs but is seasonally dependent.
7.	Manghopir spring	At tomb of Manghopir, 16 km north of Karachi on Manghopir road.	The water at the source is arrested in the form of tanks.
8.	Chasma colony spring	Near Chasma colony, Orangi Town, 12 km north of Karachi	The water at the source is arrested in the form of small tanks and the discharge balances the amount withdrawn.
9.	Gondboridge spring	Near Goth Siddique, 16 km north of Hub Chowki on RCD Highway.	Not a regular spring, water seeps through the rocks in dry season; the discharge rate is negligible.
10.	Khadeji Nadi spring	2½ km north of Shajee hotel, about 65 km east of Karachi on Super Highway	The water at the source is arrested in the form of small ponds and the discharge balances the amount withdrawn.
11.	Goth Hanidan spring	Near Goth Hanidan,100 km north of Karachi on Hub Dam road.	The discharge rate is 4.1 cusec
12.	Bolar Nala spring	Near Dewane Shah, 175 km north of Karachi	The discharge rate is 2.6 cusec
13.	Barki Dhora spring	At Barki Dhora, 8 km north of Karachi	The water is being collected in a pond, the discharge water balances the amount withdrawn, volume of water is about 50,000 cft.
14.	Bunjo Dhora spring	65 km north of Thana Bola Khan	The water is arrested at the source in the form of a small tank, the discharge balances the amount withdrawn.
15.	Goth Ghaibi spring	8 km south of Karachi and 65 km north of Thana Bola Khan.	The water is arrested at the source in the form of a small pond, the discharge balances the amount withdrawn.
16.	Ratan Shah spring	60 km west of Karachi	Discharge rate is 2.4 cusec.

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Table 2. Characteristic/constituents of springs.

Sl. No.	pH	E.C. at 25° mmhos/cm	TDS (ppm)	Phenolph thalein (ppm)	Methyl- orange (ppm)	Total alkalinity (ppm)	Cl (ppm)	SO_4^{--} (ppm)	HCO_3^- (ppm)	Ca^{++} (ppm)	Mg^{++} (ppm)	Na^+ (ppm)	K^+ (ppm)
				Alkalinity as $CaCO_3$									
1.	8.75	2.378	1130	60	380	440	225	129	390	30	32	280	18
2.	7.75	15.02	7896	zero	340	340	3446	1560	332	449	457	1725	20
3.	8.15	2.8003	1320	10	240	250	439	138	225	66	44	276	8
4.	8.2	2.73	1232	10	210	220	432	144	244	59	54	276	6
5.	8.1	11.33	5674	traces	190	190	1971	1320	232	157	116	1579	32
6.	8.05	1.502	682	zero	240	240	184	120	234	40	46	104	6
7.	8.0	3.141	1430	zero	320	320	394	219	312	35	39	375	14
8.	8.15	5.8	2760	traces	280	280	978	470	274	112	105	625	28
9.	8.1	4.64	2090	zero	420	420	765	224	410	90	84	490	11
10.	8.0	1.09	610	zero	260	260	128	41	254	46	35	80	3
11.	8.4	1.639	726	10	140	150	213	171	127	45	40	125	8
12.	8.25	2.185	968	10	260	270	235	130	244	51	61	129	4
13.	8.5	2.595	1088	20	280	300	311	178	254	42	63	195	13
14.	8.3	1.366	715	zero	340	340	99	66	332	59	35	80	6
15.	7.9	1.775	826	zero	290	290	198	113	275	96	34	92	8
16.	8.45	1.6396	756	20	240	260	156	117	214	48	52	83	3

investigation are located, are composed mainly of sedimentary rocks which have a higher solubility in water compared with igneous rocks. These rocks therefore furnish a major portion of the soluble constituents to ground water[8]. Sodium and calcium are the commonly added cations while bicarbonates, carbonates and sulphates are the corresponding anions from these sources; chlorides occur only to a limited extent under normal conditions. Before dealing with the variation in chemical composition and the quality of the spring waters it might be pertinent to describe the geological formations of Karachi and its neighbourhood.

The area under reference comprises three main geological formations, namely the Gaj, Nari and Manchar. The Nari formation comprises mainly calcareous sandstone, shale and marls having minor constituents whereas Gaj formation has sandstone, shale and some conglomerates. Sandstone, shale, limestone and conglomerates are the main rocks while calcite found in joint planes of limestone and gypsum found overlying the Gaj formation are the associated minerals. Sandstone and shale are interbedded as strata 0.3 to 7.5 metres thick. The lower half of the formation is predominantly sandstone while the upper half has mainly shale, and its proportion increased towards the sea coast.

The soil of the region is calcareous and at a few places it has a definite zone of lime accumulation. Its pH ranges between 8.2 and 8.4 and the organic matter content is quite low. The average rainfall here is 100 to 250 mm.

The pH value of the springs as listed in Table 2 ranges between 7.75 and 8.75 with 12 out of 16 springs having values above 8.0. Most ground waters have values between 5.0 and 8.0, those above 8.5 are usually associated with sodium carbonate-bicarbonate waters, while moderately high values are common for water high in bicarbonate content.

The slight increase in conductivity of spring water sample No. 6 may be due to low bicarbonate content, while the decrease in that of samples 10, 14, 15 and 16 may be due to dissolved or uncombined gases and higher bicarbonate content. The noted increase in conductivity after boiling, especially in samples 2 and 5 is apparently due to high concentration of sodium, magnesium, calcium, chloride and sulphate ions.

The data listed in Table 2 suggest that these waters are from sedimentary rocks. The higher content of chloride ion is perhaps due to the presence of ancient sea water entrapped in sediments, solution of halite and related minerals in

evaporite deposits or concentration of ingredients contributed by precipitation[9].

The source of sulphate in the spring waters is mainly calcium sulphate and sodium sulphate to a limited extent. The period of contact of water with sulphate minerals in the acquifer is practically the only governing factor with respect to the dissolved sulphates present in water.

Magnesium is contributed to these waters by dolomite while calcium is done by calcite, aragonite, gypsum etc. Ground waters in contact with sedimentary rocks of marine origin derive most of their calcium from the calcite, aragonite, dolomite, anhydrite and gypsum mix[10].

It may be noted from Table 2 that spring waters with low TDS are rich in bicarbonates, the trend being reversed as the concentration of the former increases. Sulphate concentration corresponds with TDS; it tends to increase and decrease with a rise or fall in TDS; it is after a certain limit that the trend is unpredictable. Similarly the chloride ion concentration increases with a rise in TDS. The pattern of variation in concentration of the ingredients just noted are in accord with the studies of A.V. Kovda[11].

Spring waters which can be classifed as ground water are essentially a seven component aqueous system constituting Na^+, K^+, Ca^{++}, Mg^{++}, Cl^-, HCO_3^- and SO_4^{--} ions. The dissolved matter, although originating from the minerals in the aquifer has no relation with the composition of the rocks. It is the soluble impurities occurring in rocks which affect the water quality and thus render it out of proportion to their overall mineral composition. The nature of rocks therefore is only one of the many factors affecting water quality[6]. In fact a correlation between water quality and rock types is hard to derive in all areas since the chemical composition of ground water/spring water may change during circulation as a result of leaching, dilution, reaction, concentration and ion exchange.

Table 3 lists the cation and anion contents of the spring waters under investigation. The values are expressed in milli-equivalents per litre ($meql^{-1}$). The samples may be classified into three main categories on the basis of their ionic composition:

Type I   : CO_3 comb. $> Cl > SO_4$ and $Na > Mg > Ca > K$
Type II : $Cl > CO_3$ comb. $> SO_4$ and $Na > Mg > Ca > K$
Type III: $Cl > SO_4$ CO_3 comb. and $Na > Mg > Ca > K$

The samples namely 10 and 14 are of type I. In sedimentary rocks, fresh waters are located in siliceous sands and sand stones, essentially formed by quartz. Their ionic composition is $Ca^{++} > Na^+ > Mg^{++}$ and CO_3 comb. $> Cl > SO_4$ but Na^+ may exceed Ca^{++}[12]. These two samples are true carbonate waters since the CO_3^{--} combined ($HCO_3 + CO_3$), in both samples is higher than all the other

Table 3. Contents of cations and anions in spring waters, radical expressed in Meq/lit.

S.No.	Ca^{++}	Mg^{++}	Na^+	K^+	Cl^-	SO_4^{--}	$(HCO_3^{-} + CO_3^{-})$*
1.	1.48	2.63	12.18	0.46	7.16	2.68	6.39
2.	22.2	37.56	75.03	0.51	96.83	32.44	5.4
3.	3.27	3.61	12.0	0.2	12.33	2.87	3.66
4.	2.92	4.43	12.0	0.15	12.13	2.99	4.0
5.	7.78	9.52	68.68	0.81	58.38	27.45	3.8
6.	1.98	3.77	4.52	0.51	5.17	2.49	3.81
7.	1.73	3.2	16.31	0.35	12.33	4.55	5.08
8.	5.55	8.62	27.18	0.7	27.48	9.77	4.46
9.	4.46	6.89	21.31	0.28	21.49	4.65	6.68
10.	2.28	2.87	3.48	0.07	3.59	0.85	4.14
11.	2.23	3.28	5.43	0.2	5.98	3.55	2.07
12.	2.52	5.00	5.61	0.1	6.6	2.7	3.97
13.	2.08	5.17	8.48	0.33	8.73	3.7	4.14
14.	2.92	2.87	3.48	0.15	2.78	1.37	5.41
15.	4.76	2.79	4.0	0.2	5.56	2.35	4.48
16.	2.18	4.26	3.61	0.07	4.38	2.43	3.48

*CO_3 is present in traces only.

cations and anions which is a characteristic of carbonate water.

The samples namely 1, 3, 4, 6, 7, 9, 12, 13, 15 and 16 may be placed in type II but their composition could initially be taken as of type I i.e. CO_3 comb. $> Cl > SO_4$ and $Na > Mg > Ca > K$ which in the ultimate has changed to type II under the influence of salinity.

The remaining four samples namely 2, 5, 8 and 11 are of type III; $Cl > SO_4 > CO_3$ comb. and $Na > Mg > Ca > K$. The latter also seem to be basically carbonate type which due to the presence of salts retained by adsorption on colloidal particles of clay at the time of sedimentation may have become high in total saline matter/total dissolved solids, SO_4 and Cl having higher concentration than CO_3 comb. The generally high SO_4 content of the waters might be due to high Ca^{++} and $Mg++$ content, while the Cl and Na content have a parallel development. Evaporation and a consequent concentration may also have contributed to selective precipitation of $CaCO_3$ in the form of concentrations in soils, followed by $CaSO_4$ and finally Na_2CO_3 and Na_2SO_4 depending on the CO_3 and SO_4 content of the mother liquor. Concentration of carbonate water in successive stages leads to the ultimate composition: $Na > Mg > Ca > K$ and $Cl > SO_4 > CO_3$ comb. It may be noted that the cationic composition of almost all the samples follows the sequence $Na > Mg > Ca > K$.

The analysis and classification of the spring waters suggests that they are mainly carbonate waters under the influence of main sedimentary rocks. Most of them are located in arid or semi-arid areas where evaporation and low rainfall have led to increase in total dissolved solids. Some of these areas being located near the coastal strip have been influenced by sea water intrusion and have become enriched in ions characteristic of saline water.

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