Nitrate/Nitrite Contamination in Groundwater of Karachi and its Correlation with other Physicochemical Parameters

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Summary: A study on the contamination of groundwater by nitrate and nitrite in residential areas of all the five districts of Karachi has been conducted. Samples have been analyzed for their different chemical constituents and nitrate/nitrite content. The mean concentration of all the major chemical constituents like calcium, magnesium, sodium, potassium, chloride and sulfate were found to be particularly higher in groundwater samples of district South. In the light of this study, groundwater samples of Karachi have been characterized as hard water. Nitrate contents were within the range of 0.4 – 44.5 ppm as nitrogen and 75% samples have been found to be within permissible limits of WHO guidelines for nitrate, whereas nitrite contents were found to be below detection limits in 31% (10 out of 32) of samples, however the maximum i.e. 1.69 ppm as N was found in district South. Correlation coefficients have also been calculated, however no significant correlation has been found to exist between nitrate contents and other physicochemical parameters determined in this study.

Introduction

The saturated subsurface zone (phreatic zone) contains the largest source of unfrozen fresh water in the world. It constitutes 21% of all the world's freshwater and 97% of all the unfrozen freshwater on the earth. The contribution of ground water to the total water supply is largest in arid and semiarid regions and in some places where geological condition favors the groundwater storage [1]. Ground water is a major source of water for many individuals as well as industrial units in Karachi city. The shortage of water has forced the people of this mega city of Pakistan to meet their requirements from ground water sources viz. wells, borings and hand pumps [2]. However, ground water system has become a convenient sink for toxic, industrial and domestic wastes specially in old areas and areas adjacent to industrial zones like SITE, KIA of the city. This activity has deteriorated the quality of groundwater of Korangi/ Landhi industrial area [3], and may lead to a serious threat to pollution of subsurface water in other areas of the city. The organic matter, the most abundant part of domestic and industrial waste, is decomposed by bacteria and other microorganisms under anaerobic conditions to CH_4, CO_2, NH_4^+, HCO_3^-, S^{--} etc [4]. NH_4^+ ion is slowly oxidized to nitrite (NO_2^-), which in turn is oxidized to nitrate (NO_3^-).

Nitrate is toxic to human beings when present in excessive amounts in drinking water. The most potent health effect of high nitrate levels in water is methaemoglobinaemia, (Blue baby syndrome) in infants up to 6 months of age [5]. It is also the main cause of exceptionally high 7 – 8% mortality rate among the affected infants [6]. Other adverse effects of nitrate on human health are cancer and spontaneous abortion [7, 8]. Similarly, nitrite which is mostly produced either due to reduction of nitrate and/or oxidation of ammonia, is not only considered to be the etiologic agent of methaemoglobinaemia, but also plays its role in the production of carcinogenic nitrosamine [9].

Several studies have reported, that nitrate is a potent indicator of pollution [10-12]. In Senegal, positive correlation between the levels of NO_3^-, Cl^- and colon Bacilli has been reported [10]. In Agra city, nitrate contamination was supposed to be linked to surface disposal of sewage and irrigation waste [11]. Elevated levels of nitrate were reported in the wells of rural New York which were either shallow, dug or located in large farms [12].

The quality of ground water in Karachi city has been badly affected both chemically as well as microbiologically due to the mixing of seepage of domestic and industrial wastewater with ground water from leaking sewerage lines. Because of infiltration of wastewater into ground water due to inadequate sanitation and deteriorated sewerage system, the population fed on well water is at high health risk. Hence this study is aimed to assess the

chemical quality and particularly the nitrate and nitrite contamination of ground water of the five districts of Karachi and also to determine their correlation with various measured physico-chemical parameters.

Results and Discussion

Analytical data of water samples collected from various locations of five districts of Karachi namely East, West, Malir, Central and South is presented in Table-1. It may be observed that pH of these water samples ranges between 6.8 – 8.0, which is within the permissible limits of WHO guidelines [13].

The mean concentration and ranges (given in parentheses) in mg/L for major cations and anions in all the five districts of Karachi are: calcium 78 (17-645), magnesium 87.5 (15-478), sodium 607 (63-2700), potassium17 (3-112), chloride 676 (73-4738) and sulfate 352 (66-1854). The levels of all these ions are comparatively higher in district South, where the mean concentrations have been found to be 220, 163, 1419, 43, 20, 90, 742 mg/L for Ca, Mg, Na, K, Cl, SO_4 respectively (Table 1). This may be due to the fact, that this particular district is quite close to the sea.

The hardness value of ground water samples of Karachi ranges between 204-1078 mg/L as $CaCO_3$

Table 1:Chemical Quality of Groundwater Samples Collected from Five Districts of Karachi.

I.D.	pH	Ca^{++} (ppm)	Mg^{++} (ppm)	Na^{+} (ppm)	K^{+} (ppm)	Cl^{-} (ppm)	SO_4^{--} (ppm)	TDS (ppm)	Hardness as $CaCO_3$ (ppm)	Alkalinity as $CaCO_3$ (ppm)	NO_3^- as N (ppm)	NO_2^- as N (ppm)	PO_4^{---} as P (ppm)
District East													
1	7.3	76.9	16.5	62.5	10	72.6	70	596	260	235	1	0.011	0.218
2	7.0	84.2	48.2	450	19.5	398	255	1769	408	421	31.7	BDL	BDL
3	7.5	101	74.9	362.5	22.5	845	206	2150	560	441	21.8	0.136	BDL
4	7.2	113	193.6	1037	12	1453	704	4087	1078	470	17.1	0.016	BDL
5	7.3	62.5	38.4	340	13.5	337	218	1428	314	343	1.45	BDL	BDL
6	7.5	27.2	33.3	152	9.5	106	115	802	204	294	1.7	0.272	BDL
7	7.6	38.5	73.9	400	7.5	409	98.9	1734	400	588	3.9	0.015	BDL
8	7.7	61.7	87.1	425	12	409	243	4086	521	539	29.2	BDL	BDL
9	7.3	44.1	146.9	456	12	647	275	2239	788	539	40	0.185	BDL
10	7.8	64.9	36.5	155	7	156	91	916	312	333	0.4	BDL	BDL
11	8.0	65.3	35	140	6.5	121	115	901	308	343	9.75	0.017	BDL
Average	7.46	69.2	66.4	309.7	12.3	373.8	204.5	1633	454	413	12.7	0.175	0.012
Maximum	8.0	146	209	1037	23.5	1453	704	4087	1078	588	40.0	0.272	0.218
Minimum	7.0	27	16.5	62.5	5.5	72.6	70.0	596	204	235	0.4	BDL	BDL
District West													
1	7.7	231	61.3	487.5	6.5	429.6	953	2528	828	294	24.3	0.011	BDL
2	7.7	353	300	2500	19.5	4391	927	8622	2115	109	3.65	BDL	BDL
3	7.4	122	73	500	47.5	759.3	325.5	2258	604	353	11.1	0.273	BDL
4	7.9	16.8	19.9	222.5	3	106.5	65.9	842	124	333	8.6	BDL	BDL
Average	7.7	180.6	113.6	927.5	19.1	1421.6	568	3562	918	272	11.9	0.071	-
Maximum	7.9	353	300	2500	47.5	4391	953	8622	2115	353	24.3	0.273	-
Minimum	7.4	16.8	19.9	222.5	3	106	65.9	842	124	109	3.65	BDL	-
District Malir													
1	7.3	96.9	62.7	182.5	12	198.8	140.1	1303	500	500	31.2	0.008	BDL
2	7.5	115	117	912	13.5	1023.5	556.2	3240	768	412	29.7	0.218	BDL
3	7.5	56.1	65.7	425	8	445.7	177.2	1898	410	549	7.75	BDL	BDL
4	7.4	59.3	25.8	125	26.5	165.1	98.9	764	254	216	1.45	0.381	0.111
5	7.7	41.7	16.5	90	10.1	88.8	74.2	536	172	176	1	0.022	BDL
Average	7.5	73.4	57.5	347	14	384.4	209.3	1538	421	371	14.2	0.126	-
Maximum	7.7	115	117	912	26.5	1023.5	556.2	3240	768	549	31.2	0.381	-
Minimum	7.3	41.7	16.5	90	8	88.8	74.2	536	172	176	1.0	BDL	-
District Central													
I.D.	**pH**	**Ca^{++} (ppm)**	**Mg^{++} (ppm)**	**Na^{+} (ppm)**	**K^{+} (ppm)**	**Cl^{-} (ppm)**	**SO_4^{--} (ppm)**	**TDS (ppm)**	**Hardness as $CaCO_3$ (ppm)**	**Alkalinity as $CaCO_3$ (ppm)**	**NO_3^- as N (ppm)**	**NO_2^- as N (ppm)**	**PO_4^{---} as P (ppm)**
1	7.0	85.8	56.4	135	12	112	103	1120	446	490	17.1	0.006	BDL
2	7.8	43.3	90.9	737	10	726	420	2698	482	549	9.75	0.0075	BDL
3	7.4	65.7	48.2	535	6.5	525	420	2030	362	353	13.55	0.392	BDL
4	7.6	165	76.4	565	6.5	944	338	2418	726	265	12.2	BDL	BDL
5	8.0	100	90.9	350	6	745	226	1830	624	255	10.55	BDL	BDL
6	7.5	36.9	65.2	250	9	251	165	1292	360	421	2.6	0.0119	BDL
7	7.5	64.9	32.1	330	7.5	270	173	1380	294	412	10	0.0194	BDL
Average	7.5	80.3	65.7	414.6	8.2	510.6	263.5	1821	471	392	10.8	0.062	-
Maximum	8.0	165	90.9	737	12	944	420	2698	726	549	17.1	0.392	-
Minimum	7.0	36.9	32.1	135	6	112	103	1120	294	255	2.6	BDL	-
District South													
1	7.6	198	118	2950	73	4738	798	9222	684	284	13.2	0.006	BDL
2	7.5	103	77.8	275	23	416	441	1550	576	176	0.95	1.69	BDL
3	7.3	111	126	738	112	812	400	3661	795	1117	21	0.039	1.26
4	6.8	645	478	2700	3	4011	1854	10194	3575	412	44.5	0.039	BDL
5	7.3	43.3	14.6	430	6	475	218	1617	168	353	31.2	BDL	BDL
Average	7.3	220	163	1418.5	43.4	2090.4	742	5428.8	1160	468	22.2	0.355	-
Maximum	7.6	645	478	2950	112	4738	1854	10194	3525	1117	44.5	1.69	-
Minimum	6.8	43.3	14.6	275	3	416	218	1550	168	176	0.95	BDL	-
WHO Guidelines for Drinking Water													
	6.5 -8.5	No value	No value	200	No value	250	250	1000	No value	No value	10	0.9	No value

for district east,124 – 2115 mg/L as $CaCO_3$ for district west, 172 - 768 mg/L as $CaCO_3$ for district Malir, 294 – 726 mg/L as $CaCO_3$ for district Central and 168 – 3525 mg/L as $CaCO_3$ for district South. Water is characterized as very soft, if its hardness is <15 mg/L as $CaCO_3$, soft when it ranges 15 - 50 mg/L, medium hard when 50 - 100 mg/L, hard when 100 – 200 mg/L and very hard when it is >200 mg/L as $CaCO_3$ [14]. On the basis of our findings, ground water of Karachi city may be characterized as hard to very hard water.

Table 1 shows that Total Dissolved Solids (TDS) in these samples ranges between 536 and 10194 ppm and on the basis of TDS, only 31% samples (10 out of 32) have been found to be potable (fit for human consumption), as per WHO guidelines [13]. The comparison of average salt (NaCl) and TDS contents in all five districts [Fig.1], shows that maximum salt and TDS contents are in the samples of district South, which might be due to sea water intrusion in groundwater. As this particular district is quite nearer to the sea as compared to the other four districts. It may also be seen in Fig.1, that the chemical quality of ground waters of districts Malir and East is almost the same, the TDS load is better as compared to other districts.

Table-1 also shows that the nitrate content of ground water samples of Karachi region generally ranges between 0.4-44.5 ppm as nitrogen. Highest concentration of nitrate was however found in district South, whereas lowest was found in the district East. The data detailed in Table-1 further shows, that out of a total of thirty two underground water samples analyzed in this study, nitrate content in twenty four water samples (75%) has been found to be within the permissible WHO limits [13].

Nitrite contents of the ground water samples of all the five districts of Karachi region are within the WHO permissible limits i.e. 0.9 mg/L as Nitrogen except one i.e. sample No.2 in district South, ranges as low as below the detection limits of the analytical procedure (0.05 mg/L as N) to as high as 1.69 mg/L as N, which, like that of nitrate is again for district south (Fig. 2).

In order to find out a correlation between the nitrate contents and other physicochemical parameters, correlation coefficients have been calculated and results are given in Table-2. A review of Table-2 shows, that there is a strong positive correlation between the different cations and anions present in the water samples like sulfate(SO_4^{--}), chloride(Cl^-), sodium(Na^+), calcium(Ca^{++}) and magnesium (Mg^{++}). These results also show, that these cations and anions are strongly correlated to one another in the basic composition of water. Further, phosphate(PO_4^{---}) and potassium(K^+)contents are strongly correlated to one another, suggesting that several instances of phosphate contamination in the groundwater samples

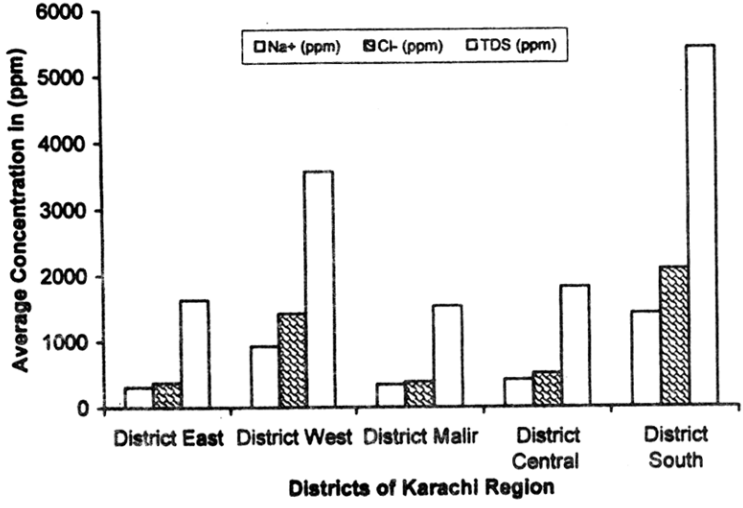

Fig. 1: Major Chemical Constituents in ground water samples of Karachi.

Table-2:Correlation Coefficients between Different Physicochemical Parameters of Groundwater Samples of Five Districts of Karachi

	NO_3^-	NO_2^-	PO_4^{---}	SO_4^{--}	Cl^-	Ca^{++}	Mg^{++}	Na^+	K^+
NO_3	1								
NO_2	-0.18989	1							
PO_4	0.043875	-0.04344	1						
SO_4	0.447344	0.01965	-0.01137	1					
Cl	0.214776	-0.10371	-0.03123	0.781829	1				
Ca	0.38922	-0.05306	-0.01239	0.923417	0.772822	1			
Mg	0.437404	-0.05145	0.040916	0.875326	0.77964	0.887463	1		
Na	0.273851	-0.12266	-0.00136	0.825135	0.987668	0.781116	0.794952	1	
K	0.027384	0.076861	0.771539	0.099036	0.298446	0.054511	0.074519	0.305429	1

collected from different localities of the Karachi city may be due to the injudicious use of fertilizers [15]. However, no significant correlation is found between the nitrate contents and other chemical parameters determined in our study.

Nitrate contamination in groundwater basically originates from a number of sources including extensive use of nitrogenous fertilizers or leaching from open disposal of agricultural, animal and human wastes [16-19]. Correlation found between chloride (Cl^-) and nitrate(NO_3^-) indicates, that nitrate contamination arises mainly from human and animal waste. If high nitrate content of subsur-face water is observed with high potassium contents, it is considered to be mainly caused by the use of fertilizers [15]. No such correlation has however been found in this study between nitrate contents with that of potassium(K^+) or chloride(Cl^-) contents. It may therefore been inferred that, nitrate content in the water of this area is arising from both the sources of fertilizers as well as contamination from animal and human waste [8]. However when correlation study was conducted, on different chemical parameters of water samples and nitrate collected from all five districts independently (Table-3), ground waters of district East and Malir, showed a positive correlation between their chloride (Cl^-) and nitrate(NO_3^-) contents, (0.444 and 0.57 respectively). This fact also leads to the conclusion, that nitrate contribution may arise from the contamination of human/animal waste in these two districts. Positive correlation has also been obtained between potassium (K^+) and nitrate(NO_3^-) 0.536 in district East, indicating agro-related activities in this district.

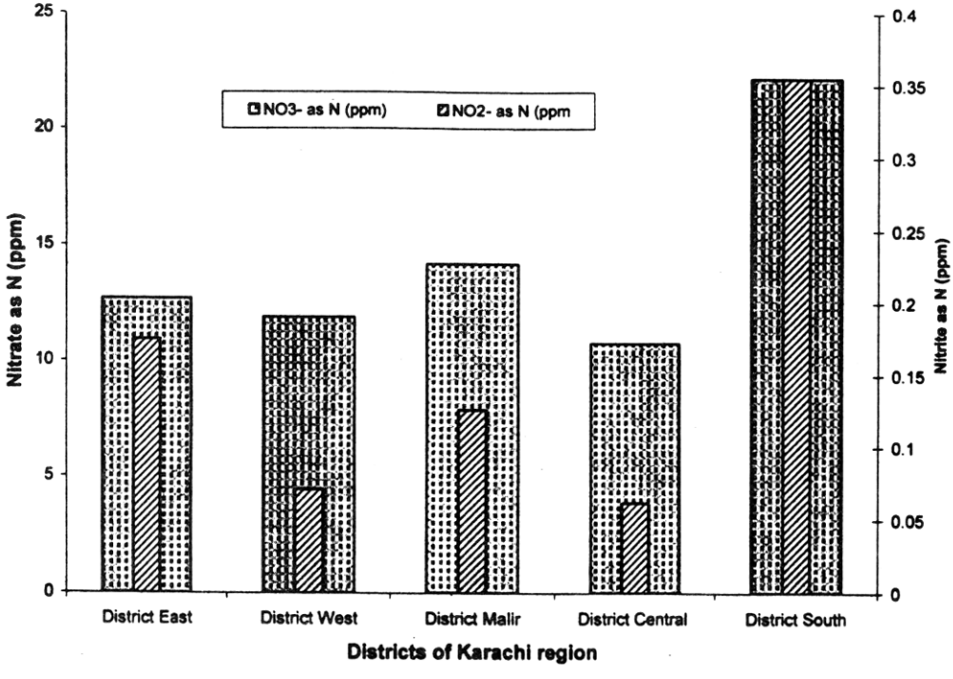

Fig. 2: Average Nitrate/Nitrite Levels in groundwaters of Karachi.

Table-3:Correlation of Nitrate (NO_3^-) with other Chemical Parameters of Groundwater Samples of Five Districts of Karachi.

	NO_3^-	NO_2^-	PO_4^{---}	SO_4^{--}	Cl^-	Ca^{++}	Mg^{++}	Na^+	K^+
Dist. East	1	0.145	-0.308	0.411	0.444	0.209	0.562	0.450	0.536
Dist. West	1	0.023	-	0.313	-0.604	-0.055	-0.552	-0.564	-0.242
Dist. Malir	1	-0.163	-0.474	0.637	0.568	0.946	0.795	0.567	-0.251
Dist. Central	1	0.254	-	0.073	0.021	0.445	-0.16	-0.023	0.162
Dist. South	1	-0.705	-0.039	0.603	0.296	0.658	0.656	0.358	-0.364

Experimental

Sampling

Samples were collected in one liter polyethylene screw capped bottles, pre-cleaned with detergent, washed with plenty of tap water, and finally with de-ionized water. After cleaning operation, blanks for each bottle were prepared in deionized water and bottles having detectable levels of nitrate and nitrite were rejected. Sample bottles were then dried at 50°C, cooled to room temperature, recapped and labeled. Samples for phosphate (PO_4^{---}) estimation were collected in acid washed glass bottles. Groundwater samples collected from all the five districts of Karachi were brought to the laboratory and immediately stored at -20°C and analyzed as soon as possible. All necessary precau-tions were observed while sampling, and also during their transportation and storage [20].

Analytical Procedures

A.R grade chemicals were used in the preparation of reagents and standards. Physico-chemical analysis was performed for each sample in triplicate and the average values were recorded. pH was measured immediately after collection of each sample using pH meter (Griffin pH meter Model 65). All other analyses in this study were completed within 48hours time after sampling. Sulfate (SO_4^{--}) and total dissolved solids(TDS) were determined gravimetrically, chloride by argentometric titration, alkalinity by acidimetric titration with HCl to pH 4.5 and calcium (Ca^{++}) and magnesium(Mg^{++})were determined by EDTA titration method whereas sodium (Na^+) and potassium (K^+) were determined by flame photometer. Furthermore phosphate (PO_4^{---}) and nitrite (NO_2^-) contents were analyzed spectrophotometerically [20]. Nitrate(NO_3^-) in ground water samples was determined by Brucine sulfanilic acid method [21].

Conclusions

It may be concluded from this study that on the basis of chemical composition, the ground water for Karachi may be characterized as saline as well as brackish water. Factors such as low rain fall, sea water intrusion, ion exchange and evaporation/ concentration have influenced the chemical composition of ground water. High levels of TDS particularly in the samples of district South may be attributed to sea water intrusion. The high nitrate content in around 25 % water samples, collected from the five districts of Karachi, make them unsuitable for human consumption. Furthermore it is suggested, that threshold limits of nitrate and nitrite levels in water samples should also be pre-checked in addition to their total dissolved solids (TDS) and microbiological aspects before recommending for their potability or otherwise.

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