Groundwater Quality of District Tharparkar, Sindh, Pakistan: Focus on Fluoride and Fluorosis

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Summary: The concentration of fluoride (F) in groundwater samples of district Tharparkar was determined, which is the largest arid region of Sind province. Various other water quality parameters such as pH, EC, TDS, Ca, Mg, Na, K, Cl, SO_4, HCO_3, were also measured. On the basis of these results, the groundwater of dist. Tharparkar can be characterized according to Rabinove, *et al.*, classification of salinity as moderately to highly saline and according to Durfor, Beaker's classification of total hardness, these samples may be characterized as hard to very hard. A systematic calculation of correlation coefficient among fluoride and other physicochemical parameters was performed, a significant –ve correlation was observed for F and Ca, Ca/ F ratio, Mg, HCO_3, & Cl contents of district Tharparkar. The fluoride concentration in the groundwater samples of this region varied from (0.93–11.8) mg/ L. 27 samples out of 33 were found to have higher fluoride contents as compared to WHO Guideline value of 1.5 ppm. These elevated levels of fluoride are putting the population at a high risk of dental and skeletal fluorosis and other severe problems associated with fluoride.

Introduction

Fluoride occurs fairly abundant in the earth's crust. The soil at the foot of the mountains is particularly high in fluoride contents due to the weathering and leaching of bedrocks with high fluoride contents [1]. Since some fluoride compounds in the earth's upper crust are soluble in water, fluoride is found naturally in both surface and groundwater. In surface fresh water, however fluoride concentrations are usually low i.e. 0.01 to 0.3 ppm [2]. The major sources of fluoride in groundwater are fluoride bearing rocks such as fluorspar, cryolite, fluorapatite and hydroxylaptite [3] However the natural concentrations of fluoride depend upon the geological, chemical and physical characteristics of the aquifer, the porosity and acidity of soil and rocks, the temperature, the action of other chemical elements like calcium and bicarbonates and the depth of the well *etc.* [4-5]. Because of the large number of variables, the fluoride concentration in groundwater can range from well under 1 ppm to more than 35 ppm [6].

Fluoride ingestion in the human body takes place *via* food, water, industrial exposure, drugs, cosmetics etc. However drinking water is the major contributor (75–90) % of daily intake [7]. In certain commodities, fluoride is purposely added to water supplies, tooth pastes and some other products to promote dental health as there is clinical evidences ithat fluoride inhibits enzyme that feed acid producing bacteria and due to its strong electro-negativity, fluoride is attracted by positively charged Ca in teeth and bones, strengthening them at the time of their formation [8].

More recently, scientists are now debating whether fluoride confers any benefit at all and how to avoid its over exposure. The major health based issues related to excessive fluoride intake are kidney and bladder disorders, skin diseases, calcified deposits in the aorta, interference with thyroid function causing hypothyroidism and weakening of immune system, damage to connective tissue collagen to ligaments, tendons, bones, arteries and DNA, fluoride even at 1 ppm or less inhibits the operation of 100 different enzymes in the cell [9].

Evidence for high levels of fluoride in groundwaters and surface waters in the rural areas of Sind is known to the authors but none of them has been reported. This paper presents the first ever baseline data on fluoride in groundwater of district Tharparkar, Sindh, Pakistan.

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Results and Discussion

District Tharparkar is situated between 24°10' - 25°40' Latitude and 69°04' - 71°06' Longitude. It lies in the south eastern arid zone of Sind which is spread at an area of about 22,000 sq km and inhabited by above one million in people. The study was undertaken in all the three talukas namely Chachro, Mithi and Diplo of district Tharparkar.

The groundwater samples collected from the studies area had almost no color, odor and turbidity, however taste of these water samples was brackish. The physicochemical parameters analyzed for the groundwater samples, collected from district Tharparkar with their location and comparison with WHO guidelines are summed up in Table-1 and it shows that 81 % (27 out of 33) water samples due to their quite higher salt contents, are not acceptable to be used for drinking purpose.

According to salinity classification of Rabinnove *et al.*, (Table-2) [10], these samples are non saline at 6 locations, slightly saline at 13 locations, moderately saline at 10 locations and even highly saline at 4 locations, while according to Durfor and Beakers classification of total Hardness [11], all of these samples are classified as very hard at all the locations. The value of alkalinity is more than 200 ppm as $CaCO_3$ in 75 % of the samples. All

Table-1: Physicochemical properties of groundwaters of district Tharparkar.

S.ID.	Location	pH	Ca	Mg	Na	K	Cl	SO_4	HCO_3	Total Hardness*	Total Alkalinity*	TDS	EC
1	Hali Pota Poring No. 1	7.4	280	180	3200	18	1230	4580	840	1441.6	688.8	10420	16.07
2	Virawah	7.8	300	190	2300	15	1070	3390	780	1532.8	639.6	8110	15.57
3	Murid Khan Umarani	8.0	60	40	320	9	180	560	210	314.8	172.2	1450	2.5
4	Bhirato	7.9	290	188	2280	20	1100	3341	760	1499.56	623.2	8020	15.29
5	Modoor	7.2	180	105	1214	8	590	1800	510	882.6	418.2	4480	8.41
6	Layakhro	7.1	288	240	3000	12	1560	4208	980	1708.8	803.6	10400	20.56
7	Amin Ji Dhani	7.2	240	120	1820	22	910	2540	690	1094.4	565.8	6400	12.4
8	Ismail Sangrase	7.3	58	38	380	13	180	540	254	301.56	208.28	1500	2.6
9	Aroki	7.1	120	68	740	18	360	990	610	580.16	500.2	2940	4.92
10	Doh Maliji Jo Wandhio	7.0	48	18	150	12	90	266	140	194.16	114.8	730	1.01
11	Katho Bhel	7.6	38	16	135	8	78	202	160	160.92	131.2	640	0.914
12	Kharsar	7.6	34	14	44	4	48	75	110	142.68	90.2	330	0.49
13	Vakiro	7.4	88	46	400	12	205	660	190	409.52	155.8	1610	2.98
14	Mehari Bajir	7.7	22	11	66	5	46	90	92	100.32	75.44	340	0.51
15	Lonihar	7.2	301	192	2060	10	1080	3140	710	1543.54	582.2	7510	14.45
16	Posarko	7.5	140	98	1220	8	720	1520	680	753.76	557.6	4400	8.66
17	Arniaro	7.4	70	40	400	6	220	510	302	339.8	247.64	1560	2.96
18	Veehingorga	7.6	102	58	620	9	298	840	460	493.96	377.2	2400	4.14
19	Milhraodal	7.1	170	110	1220	8	614	1810	510	878.2	418.2	4480	8.63
20	Doonijh	7.0	108	66	780	12	408	1036	480	541.92	393.6	2860	5.05
21	Khan Khanjar Reham	7.6	70	28	175	10	120	315	150	290.36	123	880	1.65
22	Udani Chachro	7.7	70	38	350	8	180	540	180	331.56	147.6	1380	2.6
23	Allah Rakhio Jo Tar	7.8	77	17	63	10	73	70	286	260	235	596	0.916
24	Peerane jo Tar	7.1	62	88	425	12	409	243	657	521	539	4086	6.28
25	Gadro	7.4	44	147	456	12	647	275	657	788	539	2239	3.44
26	Jesse e Par	7.5	353	300	2500	19.5	4391	927	133	2115	109	8622	13.3
27	Karanghi/ Kathejiveri	7.6	115	117	912	13.5	1023.5	556.2	502	768	412	3240	4.98
28	Beknar	7.1	645	478	2950	112	4738	1854	1362	3525	1117	10194	15.6
29	Almsar V Parao	7.2	165	76.4	565	6.5	944	338	323	726	265	2418	3.72
30	Tardos	7.8	645	478	2950	112	4738	1854	1362	3525	1117	10194	15.6
31	Keetar	7.1	122	73	500	47.5	759.3	325.5	430	604	353	2258	3.47
32	Mokhai	7.5	73.4	57.5	347	14	384.4	209.3	452	421	371	1538	2.36
33	Chachro	7.6	165	90.9	737	12	944	420	669	726	549	2698	4.1
	WHO Guideline Values	6.5-8.5			200		250	250		200	200	1000	
	Average	7.4	168	115	1069	189	919	1213	503	894	413	3967	6.85
	AveDev	0.24	112	82	841	13	770	1011	255	602	209	2772	4.98
	StdDev	0.28	154	117	1007	25	1257	1264	329	848	270	3332	5.83
	Skewness	0.16	1.92	1.99	0.96	3.36	2.46	1.35	0.96	1.98	0.96	0.87	0.83
	Kurtosis	-1.04	3.92	4.10	-0.48	10.9	5.38	0.87	0.93	4.07	0.93	-0.63	-0.65

All values in ppm except pH and EC (units of EC are mmhos/cm) * Values expressed as $CaCO_3$.

Table-2: Salinity classification of Rabinnove *et al.*

S. No.	Classification of groundwater	Total dissolved salts
1	Non-saline	<1000 ppm
2	Slightly saline	1000–3000 ppm
3	Moderately saline	3000–10000 ppm
4	Very saline	>10000 ppm

Table-3: Total hardness classification of Durfor and Beckers.

S. No.	Classification of groundwater	Hardness as $CaCO_3$
1	Soft	0–60 ppm
2	Moderately hard	61–120 ppm
3	Hard	121–180 ppm
4	Very hard	>180 ppm

other minerals are also present in quite high concentration in all the samples (Table-3).

The main focus of this study is however on the fluoride levels in drinking water samples from District Tharparkar and to investigate its health related issues. It has been established earlier that water borne fluoride is absorbed in the body more rapidly than food borne fluoride [12], therefore high levels of fluoride in drinking water would put the fed population at a higher risk of problems associated with fluoride. The concentration of fluoride in groundwater of the investigated area was found to be between 0.93 – 11.8 ppm with an average of 3.2 ± 2.48 ppm. The data is depicted in Fig. 1 in comparison to the WHO guidelines and it has been obvious from this study that around 82 % sample (27 out of 33) samples contain fluoride levels far above the WHO guideline values.

According to Keller [13] description as regards concentration of fluoride in drinking water and health based issues, the levels of fluoride in drinking water may be classified in 5 Zones, Zone I (< 1.5 ppm fluoride in drinking water) is of maximum benefit for teeth and bones development, zone II (>1.5 – 5 ppm fluoride in drinking water) is susceptible zone for children whose teeth and bones are in the state of formation, Zone III (>5 – 6.5 ppm fluoride in drinking water), Zone IV (>6.5 – 10 ppm Fluoride in drinking water) and Zone V (>10 ppm Fluoride in drinking water) depicts highly susceptible range of fluoride concentration towards dental fluorosis, calcification of ligaments, physiological mongolism, cancer mortality, birth defects, anemia and insomnia [14-17].

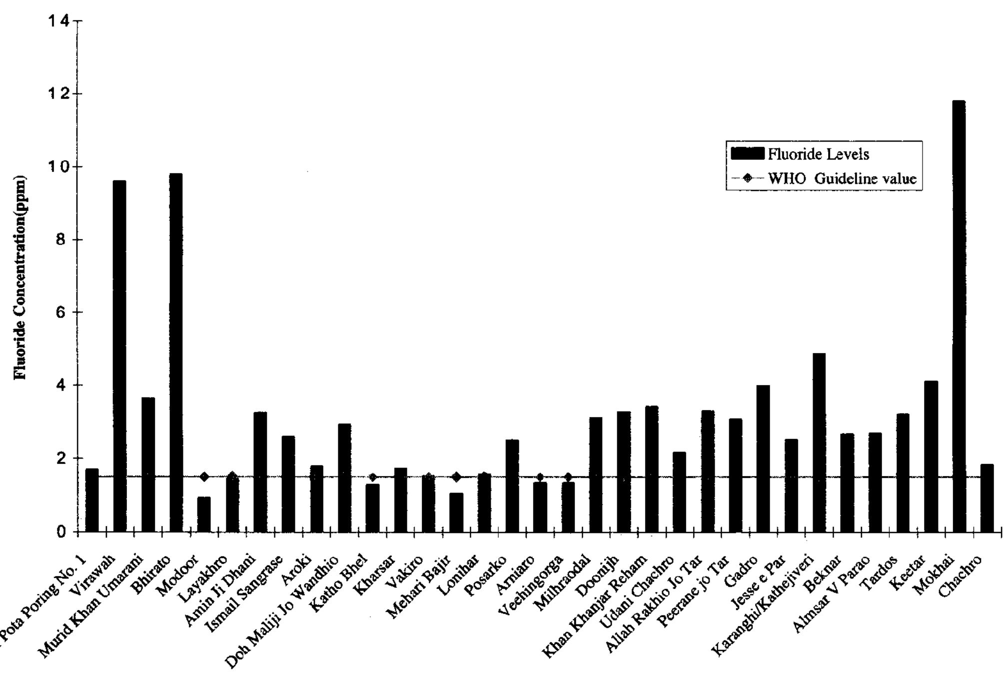

Fig. 1: Comparison of Fluoride levels with WHO Guidelines.

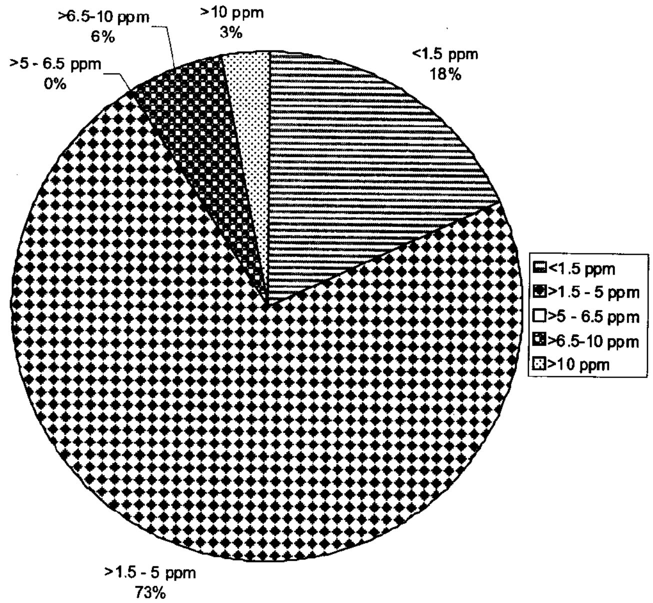

Fig. 2: Distribution of Fluoride concentration according to Keller.

The pie chart that was constructed to determine the percentage of samples lying in each zone of Fluoride concentration (Fig. 2), shows rather a disappointing picture as just 18 % samples lie in the region of maximum benefits of fluoride for teeth and bone development, while 75 % samples lie in the zone which is especially susceptible zone of fluoride concentration in drinking water for children.

A systematic regression analysis was also conducted for fluoride concentration and other physicochemical parameters as well as Ca/ F ratio and the calculated correlation coefficient are summarized in Table-4. A negative correlation exists between fluoride and other major ions like calcium, magnesium, sodium, potassium, chloride, sulfate and bicarbonate. A strong negative correlation also exists between Ca/ F ratio and it is also interesting to note that high fluoride contents are always associated with low Ca/ F ratio [3].

Table-4: Correlation coefficient between fluoride and other physicochemical parameters.

S. No.	Parameter	Correlation Coefficient
1	Calcium	-0.281
2	Magnesium	-0.226
3	Sodium	-0.359
4	Potassium	-0.101
5	Chloride	-0.245
6	Sulfate	-0.318
7	Bicarbonate	-0.158
8	Ca/ F ratio	-0.441

Experimental

Water Sampling

Ten samples of water were collected at random from each site in pre-cleaned bottles and were mixed to form a composite sample. The samples were stored in iceboxes until transportation to the laboratory, where they were analyzed within 7 days of collection. A total of 33 samples were collected from the affected areas. The correlation coefficient and other statistical parameters were determined using Microsoft Excel 2000 Program.

Methodology

All chemicals used in the study were of AR grade; the pH and EC of the water samples were determined electrometrically using Orion 701 pH meter and HAACH 2000 Conductivity/ TDS meter. Ca, Mg, Cl and HCO_3 were determined through titration with standard EDTA, $AgNO_3$ and HCl respectively. Na and K were analyzed *via* Flame photometry, SO_4 and TDS gravimetrically. All these parameters were analyzed according to APHA Standard Testing Methods [18].

Levels of fluoride were determined with Fluoride Ion Selective Electrode (VWR Cat No. 34105-116) coupled with Orion 701A digital Ion Analyzer. The calibration curve was prepared against standard NaF solutions containing 0.5, 1.0, 5.0, 10.0 and 20 ppm fluoride and it was reproducible for the whole period of study with in ± 2 % error. 5ml of Total Ionic Strength Adjustment Buffer (TISAB III commercially available) was added per 50 ml standard and sample. The graph is further checked for its accuracy by using standard 1 ppm (Orion 040906) and 10 ppm (Orion 040908) fluoride solutions. The value of slope was -52 Rel. MeV and correlation coefficient (r) = 0.9968 [18].

Conclusions

This study has highlighted the grave problem of quite high fluoride concentration in the under ground water samples of Tharparkar District. The alarming situation demands an urgent need to give attention towards de-fluoridation of drinking water presently being consumed by the majority of population, in order to prevent them from possible health hazards. Other remedial measures may be to educate the public about toxic effects of fluoride and introduction/ provision of possible low cost, household de-fluoridation techniques like lime, bone char, alum filters at their house holds.

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