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Fluoride Toxicity of Ground Water in Makrana Tehsil, Nagaur District, Rajasthan

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ABSTRACT

Habitat of Nagaur District faces large number of socio-economic and health related issues besides the usual acute shortage of potable water. The District experiences arid to semi-arid type of climate. The groundwater and a little rain for a few days in a year are the main source of water for irrigation, drinking and other domestic consumption. The quantity is low but more frightening is the quality of ground water that is being used. A survey of nineteen villages in Makrana tehsil of Nagaur district was conducted. The primary data included the study of total dissolved salts. The TDS ranged from 154 to 454 mg/l which was in most cases above the permissible limit of 200 mg/l. The other parameters studied were pH, halides (chlorides and fluorides), carbonate, bicarbonate, calcium, magnesium and some other elements. The result suggests poor groundwater quality which is highly saline (hard water) with high fluoride contents. These high fluoride levels of ground water used for drinking are anticipated to be the reasons for the prevalence of dental and skeletal fluorosis in population of this tehsil at large.

Keywords: fluoride, groundwater quality, habitat, hard water, Makrana, Nagaur, Potable, saline, TDS

INTRODUCTION

Water is the essence of life but what if it starts becoming the cause of morbidity and what if it engulfs the whole flora and fauna of the habitat. It needs serious attempts to know the reasons behind this continuing tragedy. Yes, water is life as it creates and preserves life but there are many places where high salt contamination in water is the main because of death. There are many places in the world where quantity and quality of water is threatening the survival of people. This problem is faced not only in the underdeveloped nations but also in developing nations where population growth rate is very high and base of the population pyramid is large. In the developing nations there are few places with lopsided development that lacks in the basic amenities to maintain the good living standard. It is not about the facilities of shelters or food: rather about the first and foremost basic need and pre requisite of life i.e. potable water. In water deficit Nagaur district of Rajasthan which is semi-arid and located within the Fringe of Thar Desert. It receives rain only for 20-25 days in a year (40 cm rainfall) with stabilized sand dunes and facing the acute water shortage and poor (saline) water quality both.

Quality of water is an important parameter for human health. The potable water should be free from pathogenic agents and chemical constituents, pleasant to taste and usable for human and animal consumption with other domestic purposes. The ground water is characterized by multiple quality pollutants viz., coloured dyes, heavy metals, nitrates and fluoride etc. The water is a universal solvent, which contain many dissolved substances. The preliminary study carried out in the present investigation indicates that Nagaur region contains high fluoride contamination in groundwater due to its rock structure.

Nagaur is located at 27.2°N 73.73°E. It has an average elevation of 302 metres from mean sea level. Nagaur is surrounded by seven districts namely Bikaner, Churu, Sikar, Jaipur, Ajmer, Pali, and Jodhpur in the Western margin of Aravali residuals. It is the fifth largest district in Rajasthan with a vast terrain spreading over 17,718 sq. km. Its geographical spread is a unique combination of plain, hills, sand mounds and it is a part of the great Indian Thar Desert. According to census of India 2011, Nagaur District comprises 3340044 population (male-1679570 , female-1660474) with 19.25 % decadal growth rate (2001–11).The literacy rate is 64.08 % (male literacy rate78.90% and female literacy rate 48.63%). Merta, Degana, Ladnun, Deedwana, Makarana, Parbatsar and Kuchaman are the major urban centre of the district. The total area of the district is 17,718 sq. km, out of which 17,448.5sq km is rural and 269.5 sq. km (1.52% of the total area of the district) is urban.

The Nagaur district experiences arid to semi-arid type of climate. Mean annual rainfall of the district is 410 mm whereas normal rainfall is lower than average rainfall and placed at 363.1 mm. There is significant increase in rainfall during the last 30 years. As the district lies in the desert area, it experiences scorching heat (46 degree Celsius) in summers and chilling cold (2 degree Celsius) in winters. The humidity is very high in August with mean daily relative humidity being 80%. The annual maximum potential evapotranspiration in the district is quite high and is highest in the month of May i.e. 255.1 mm and lowest in the month of December 76.5 mm.

METHODOLOGY

Sample Collection: Water samples were collected from all the existing sources of groundwater use for drinking water from varying depth of 60 feet to 420 feet in the study area for the investigation and chemical examination.

Location of sampling stations: For the present investigation, 19 samples as mentioned in the following table were collected randomly from wells, tube-wells and hand pumps for chemical analysis from different villages of the district. The Sample ID and Village Names are as follows 1. Bichava, 2. Kacholiya, 3. Spadde, 4A. Kalyanpura, 4B. Toshina, 5. NagvadaKalla, 6. Asarva, 7. Mokhumpura, 8. Kanade, 9. Basada, 10. Givadhya, 11. Mudi-charana, 14. Khurad, 15A. Geda-Kalan, 15B. Ramsiya, 16A. Jasvantpura, 16B. Nundada, 18. Naussariya, 21. Gunsuli(kiroda).

The bottles for sample collection were thoroughly cleaned by rinsing with 8M HNO_3 (nitric acid) solution, followed by repeated washing with double distilled water. They were further rinsed with sample water before collection. Physiochemical analysis was done as per standard procedure.

Sampling methods: Nineteen water samples from different sites were collected from different areas of Nagaur region. The water samples were collected from sites which are extensively used for drinking and other domestic purpose. The samples were collected in high grade plastic bottles of one liter capacity as per required procedure. The following techniques and methods were followed for collection, preservation, analysis and interpretation.

Analysis Methods: The physiochemical characteristics of the ground water samples were determined by standard reference method. The pH, Electrical conductivity, Fluoride and Nitrate were measured by using portable meters. The concentrations of Magnesium, Calcium hardness, total hardness were estimated by volumetric methods and the results were compared with the standards.

The SPADNS method for fluoride determination involved the reaction of fluoride with a red zirconium-dye solution. The fluoride combines with part of the zirconium to form a colorless complex, thus bleaching the red color in an amount proportional to the fluoride concentration

RESULTS

According to Environmental Protection Agency (EPA) one should not use water with TDS above 500 ppm. But many health specialists advises that the TDS to be below 50 ppm. But the tap water in America has nearly 350 ppm of TDS and in India although the desirable limit is below 500 ppm but where no other alternate source is found the TDS upto 1200 ppm is also permitted. In general water with TDS levels higher than 1000 ppm is not considered potable. In the present study, the TDS was found to be within 500ppm which is the acceptable level by Indian Standard of drinking water. But the electrical conductivity was very high in most of the samples studied.

In the present study the conductivity is in the range 2040-10540 µmhos/cm in sample S.No. 1 and 19 respectively. Distilled water has conductivity in the range of 0.5 to 3 µmhos/cm. Studies of inland fresh waters indicate that streams supporting good mixed fisheries have a range between 150 and 500 µmhos/cm. Conductivity outside this range could indicate that the water is not suitable for certain species of fish or macro-invertebrates. Industrial waters can range as high as 10,000 µmhos/cm. Water shows significant conductivity when dissolved salts are present in it. The hardness is due to the salts which are also included in the TDS. In this investigation, the EC is very high and its coefficient of correlation is also positive and very strong with calcium, chlorine, magnesium and fluoride .This shows that hard water has more electric conductivity. So the EC is high with moderate or acceptable TDS values. We know that over most ranges, the amount of conductivity is directly proportional to the amount of salts dissolved in the water.

Water is hard as based on the amounts of bicarbonates, calcium, magnesium and chlorides present in the samples. The calcium concentration is low as per the standards but the magnesium levels are well above ranging between 23.31 to 72.76 ppm. The sodium salts are very high ranging between 115.2 (S.No 12) and 399.2 (S.No. 5).The pH is within range (6.5 – 8.6).

Globally, fluoride in groundwater is known to contaminate the water sources. In surface waters, fluoride can occur naturally by the deposition of atmospheric derived particles and /or by fluoride-containing soils and rocks weathering and in ground water resources by leaching of rocks and soils. The problem of high fluoride content in drinking water has become a serious environmental issue in the field of water quality management and human health. Fluoride ions have dual significance in water supplies. High concentration of F^-causes dental fluorosis also called “mottled enamel” (disfigurement of the teeth). At the same time, a concentration less than 0.8 mg/L results in ‘dental caries’. Hence, it is essential to maintain the F^- concentration between 0.8 to 1.0 mg/L in drinking water. The Indian standard prescribes the limit for fluoride for water to be used for drinking as 1.5 mg/L. Chlorides, Calcium, Magnesium, and Fluoride are strongly correlated with each other and contributing in the hardness of water and high Fluoride value in water. So the EC is high with High TDS values. Ca and Mg is having positive correlation among Fluoride. That proves that all these salts are commonly dissolved in water in that area. The values of fluoride is very high and having a positive correlation with EC, Bicarbonate, calcium, Magnesium, chloride, sodium and cobalt. So, TDS, Electronic conductivity having hardness and Floride make water unfit for drinking as well as other domestic chores.

Table 1.Ground Water Sample of selected villages from Makrana Tehsil, Nagaur District, Rajasthan.

Analysis Report of Water Samples(Rajasthan)																						
		ppm	M.mhos			meq/l					ppm											
S.No	S. ID	TDS	EC	pH	CO3	HCO3	CL	Ca	Mg	Na	K	Pb	Co	Ni	P	B	S	Zn	Cu	Fe	Mn	Al	F
1	1	158	2040	7.10				19.96	42.26	285	1.14	0.009	0.001	0.006	0.04	0.85	65.98	0.04	0.04	0.021	0.012	0.07	8.50
2	2	280	5000	7.20	NIL	12.00	32.50	12.33	23.65	262.5	1.84	0.04	0.005	0.013	0.03	0.05	48.65	0.08	0.001	0.019	0.005	0.002	15.50
3	3	233	4820	8.30	0.50	15.00	35.00	21.09	39.5	310.2	0.36	0.009	0.004	0.03	0.06	0.09	46.29	0.003	0.033	0.03	0.002	0.004	11.00
4	4A	154	3170	7.20	0.50	6.50	20.00	19.05	33.45	312.3	1.53	0.003	0.003	0.002	0.01	0.03	70.97	0.001	0.018	0.012	0.006	0.0025	18.20
5	4B	157	5800	8.20	0.50	17.50	30.00	22.03	49.04	399.2	0.57	0.009	0.003	0.008	0.02	0.13	110.2	0.012	0.018	0.014	0.001	0.009	26.30
6	5	259	5640	7.30	0.50	10.00	35.00	23.23	47.92	225.6	0.09	0.002	0.001	0.002	0.02	0.09	98.43	0.04	0.018	0.007	0.006	0.02	19.00
7	6	222	6400	6.50	0.50	14.00	42.50	25.43	54.43	232.2	0.98	0.004	0.009	0.002	0.04	0.012	118	0.05	0.022	0.017	0.004	0.005	22.00
8	7	356	7100	6.60	0.50	12.00	47.50	26.76	53.27	212.3	0.81	0.001	0.008	0.012	0.003	0.012	15.73	0.008	0.025	0.014	0.004	0.039	18.30
9	8	356	7050	6.80	0.50	14.00	32.50	20.13	46.33	221.9	0.68	0.04	0.001	0.001	0.041	0.012	128.1	0.022	0.016	0.001	0.003	0.006	15.60
10	9	277	7600	8.50	0.50	20.50	30.00	11.93	29.51	198.6	0.41	0.002	0.003	0.009	0.019	0.017	94.46	0.007	0.019	0.0174	0.012	0.004	15.90
11	10	308	5500	6.60	0.50	22.50	25.00	19.62	38.18	188.6	0.18	0.03	0.001	0.009	0.007	0.016	83.26	0.17	0.092	0.008	0.003	0.001	15.30
12	11	300	4300	6.50	0.50	10.00	27.50	21.32	45.88	115.2	0.15	0.02	0.003	0.008	0.02	0.08	69.28	0.08	0.052	0.039	0.001	0.002	9.80
13	14	218	9950	8.40	0.50	17.00	60.00	23.58	65.07	214.6	0.13	0.001	0.001	0.001	0.1	0.02	261.4	0.07	0.018	0.002	0.005	0.036	16.30
14	15A	288	7700	8.30	0.50	16.00	50.00	26.87	56.63	199.7	0.41	0.002	0.007	0.001	0.003	0.01	122.6	0.05	0.022	0.007	0.005	0.012	19.80
15	15B	226	4000	8.60	0.50	5.00	19.00	4.604	34.95	215.6	1.52	0.03	0.003	0.001	1.02	0.07	45.29	0.031	0.018	0.008	0.001	0.19	18.50
16	16A	255	5700	7.40	0.50	13.00	20.00	13.55	31.46	232.1	0.63	0.008	0.001	0.009	0.14	0.01	74.61	0.02	0.017	0.002	0.009	0.18	10.30
17	16B	262	7100	7.60	0.50	5.00	35.00	32.08	70.64	365.3	0.51	0.05	0.003	0.008	0.03	0.09	143.7	0.007	0.016	0.005	0.001	0.14	11.00
18	18	450	3020	7.80	0.50	10.00	13.00	10.6	23.31	312.7	0.46	0.045	0.006	0.008	0.02	0.05	76.72	0.004	0.017	0.008	0.001	0.14	8.50
19	21	454	10540	6.70	0.50	10.00	65.00	33.08	72.76	313.7	0.11	0.03	0.009	0.012	0.06	0.099	0.04	0.011	0.0121	0.04	0.002	0.007	28.00

TDS: Total dissolved solids, **EC**: Electronic Conductivity, **pH**: Power of Hydrogen, **CO**: Carbonate, **HCO**: Bicarbonate, **CL**: Chlorine, **Ca**: Calcium, **Mg**: Magnesium, **Na**: Sodium, **K**: ,**Pb**: Lead, **Co**: Cobalt, **Ni**: Nickel , **P**: Phosphorus, **B**: Boron, **S**:Sulphur, **Zn**: Zinc, **Cu**: Copper, **Fe**: Iron, **Mn**: Manganese, **Al**: Aluminium, **F**: Fluoride.

Sample ID and Village Name: 1.Bichava, 2.Kacholiya, 3.Spadde, 4A.Kalyanpura, 4B.Toshina, 5.NagvadaKalla, 6.Asarva, 7.Mokhumpura, 8.Kanade, 9.Basada, 10.Givadhya, 11.Mudi-charana, 14.Khurad, 15A.Geda-Kalan, 15B.Ram siya, 16A.Jasvantpura, 16B.Nundada, 18.Naussariya, 21.Gunsuli(kiroda).

Table.2 Standard Limits and reference range of salts in potable water:

	Required Limit
TDS	Upto 500 ppm
pH	6.5 - 8.5
Ca	40-80 ppm
Mg	20-30 ppm
Na	20 ppm
Pb	0.01 ppm
Zn	5 ppm
Cu	0.05 ppm
Fe	0.3 ppm
Mn	0.1 ppm
Al	0.03 ppm
F	0.6-1.2 ppm

Table 3. Taste of water with different TDS concentrations:

Level of water with different TDS (milligram/litre)

Less than 300	Excellent
300 – 600	Good
600 – 900	Fair
900 – 1200	Poor
1200 and above	Unacceptable

Table 4. Inter Correlation matrix among twenty One variables.

S.NO		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
		TDS	EC	pH	HCO3	CL	Ca	Mg	Na	K	Pb	Co	Ni	P	B	S	Zn	Cu	Fe	Mn	Al	F
1	TDS	1	0.34	-0.30	-0.05	0.19	0.12	0.09	-0.16	-0.38	0.50	0.45	0.15	-0.15	-0.34	-0.31	-0.02	-0.03	0.17	-0.33	0.03	0.02
2	EC		1	0.05	0.32	0.88	0.56	0.70	-0.09	-0.49	-0.10	0.28	-0.06	-0.17	-0.44	0.34	-0.01	-0.23	-0.02	-0.08	-0.26	0.53
3	pH			1	0.10	-0.09	-0.36	-0.14	0.22	-0.02	-0.16	-0.20	0.04	0.39	-0.08	0.34	-0.31	-0.33	-0.29	0.07	0.29	-0.02
4	HCO3				1	0.18	0.00	-0.09	-0.25	-0.40	-0.35	-0.14	0.15	-0.39	-0.34	0.28	0.45	0.44	-0.07	0.36	-0.50	0.11
5	CL					1	0.74	0.80	-0.04	-0.35	-0.28	0.44	0.01	-0.25	-0.01	0.22	0.01	-0.18	0.25	-0.01	-0.42	0.53
6	Ca						1	0.88	0.20	-0.46	-0.13	0.34	0.05	-0.53	0.02	0.16	-0.04	0.04	0.23	-0.20	-0.40	0.35
7	Mg							1	0.20	-0.46	-0.13	0.34	0.05	-0.57	0.02	0.16	-0.04	0.04	0.23	-0.20	-0.40	0.35
8	Na								1	0.16	0.23	0.11	0.26	-0.13	0.22	-0.06	-0.53	-0.39	-0.01	-0.20	0.15	0.18
9	K									1	0.12	0.08	-0.13	0.38	0.19	-0.29	-0.12	-0.34	-0.11	0.16	0.19	-0.01
10	Pb										1	0.00	0.07	0.16	-0.07	-0.14	0.10	-0.03	-0.04	-0.52	0.33	-0.24
11	Co											1	0.17	-0.11	-0.24	-0.39	-0.24	-0.28	0.41	-0.29	-0.17	0.45
12	Ni												1	-0.21	0.02	-0.47	-0.14	0.13	0.53	-0.13	-0.14	-0.23
13	P													1	-0.03	-0.15	-0.05	-0.12	-0.15	-0.20	0.59	0.07
14	B														1	-0.14	-0.03	0.16	0.23	0.43	0.09	-0.29
15	S															1	0.18	-0.07	-0.56	0.05	-0.03	-0.06
16	Zn																1	0.71	-0.04	-0.05	-0.27	-0.08
17	Cu																	1	0.14	-0.05	-0.20	-0.26
18	Fe																		1	-0.12	-0.41	0.12
19	Mn																			1	-0.05	-0.21
20	Al																				1	-0.40
21	F																					1

Calculated by Computer (Ms. Excel 2010)

The Inter co-relation matrix based on variables mentioned in table. 1 clearly demonstrated that out of the 210 correlations, 195 are insignificant. Only 15 correlations are significant. The correlation matrix is required when correlation between more than two indicators is to be analyzed.

The co-relation matrix is important to find out the relation of 19 samples of water from different sites and established the corelation among 21 different variables of water. These water sample values are correlated among each other to find out their relation with other variables whether the presence of one indicator in water influence the other or not. It considers the significant values, which show correlation more than (.5) signifies positive and strong co-relation means the presence of one variable influence the presence of other variables. For example, when pb (Lead) is correlated with F (Fluoride) in water, it shows -0.24 matrix index means negatively weak correlation where Lead and Fluoride content in water are neither linked nor influencing the content in each other. In other words because of the Lead in the water Fluoride has not increased.

The relation between Phosphate – calcium and phosphate – magnesium are negative correlation(r = -0.53) and (r = -0.57) respectively. So in the case of zinc and sodium(r = -0.53). Aluminum and HNO3 also has negative correlation.it means that their occurrence is not dependent on each other. Among the 11 significant correlation, Interestingly chloride, calcium, magnesium and Fluoride are positively correlated with Electronic Conductivity such as (r = 0.88),(r = 0.56), (r = 0.70) and (r = 0.53) respectively. As we see in table 1. The EC is very high to the required level and its coefficient of correlation is also positively very strong with calcium, chlorine magnesium and fluoride. This shows that hardness of the water has more electronic conductivity. The hardness contains all the salts which included in the TDS. So the EC is high with High TDS values.

Interestingly chloride is also significantly positive co-relation with calcium, Magnesium and fluoride as (r = 0.74), (r = 0.80) and (r = 0.53) respectively. Chlorides, Calcium, Magnesium, and Fluoride are strongly correlated with each other and contributing in the hardness of water and high Fluoride value in water. So the EC is high with High TDS values. Ca and Mg is having positive correlation among Fluoride. That proves that all these salts are commonly dissolved in water in that area. The values of fluoride is very high and having a positive correlation with EC, Bicarbonate, calcium, Magnesium, chloride, sodium and cobalt. So, TDS, Electronic conductivity having hardness and Fluoride make water unfit for drinking as well as other domestic chores.

The Scatter diagram has been drawn to show the relationship among the different variables of Ground water Quality. These diagrams are based on the data collected of ground water from sample villages. this diagram signifies and visualize that the points which lies on the line of best fit have perfect correlation and other are away from the line of best fit, which shows less correlation. There are eight such diagrams have been prepared. Through these diagrams following conclusion may be drawn.

1. Electronic conductivity and TDS (Total Dissolved Solids)

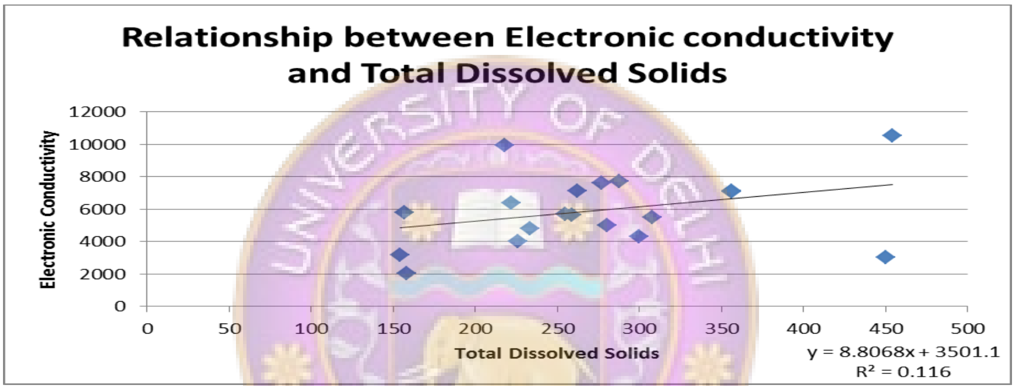


Figure I Relationship between Electronic conductivity and Total dissolved solids.

The term TDS includes all solids (usually mineral salts) that are dissolved in water. The TDS and the electrical conductivity have a strong correlation, therefore the presence of TDS quantity highly influence the Electronic Conductivity in water. . The more salts are dissolved in the water, higher is the value of the electric conductivity. Generally the water temperature affects the electric conductivity so that its value increases from 2% to 3 % per 1 degree Celsius. So, in Semi-arid regions like villages in Makrana tehsil has high temperature in the range of 15 degree Celsius to 50 degree Celsius. In such high temperature conditions the EC increases up to 10000 M.mhos so the TDS increases upto 450 ppm as a result water hardness is increased.

1. Relationship among EC, Calcium, Chloride, Magnesium, and Fluoride:

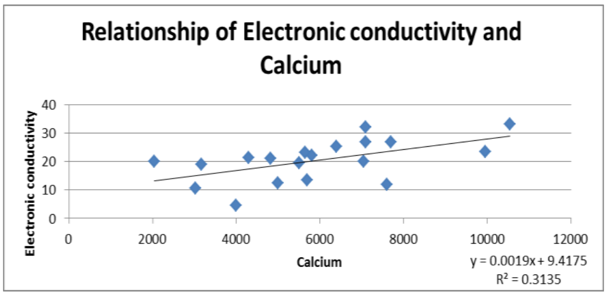


Fig. 2 Relationship between EC and Calcium.(r = .56)

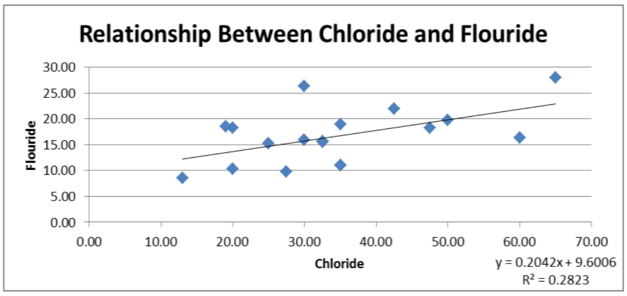
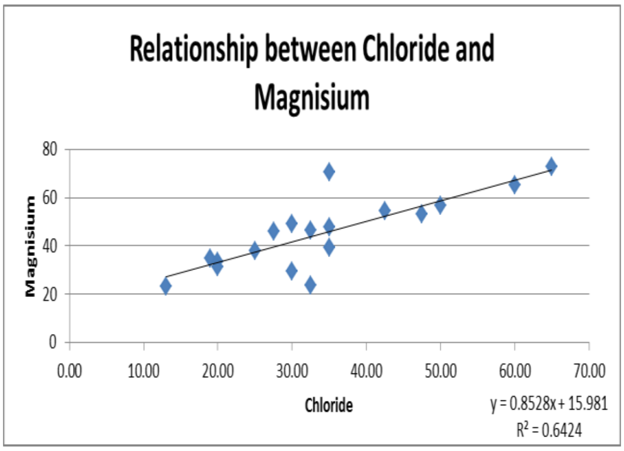


Fig3. Relationship between Chloride and Fluoride. (r =.53)



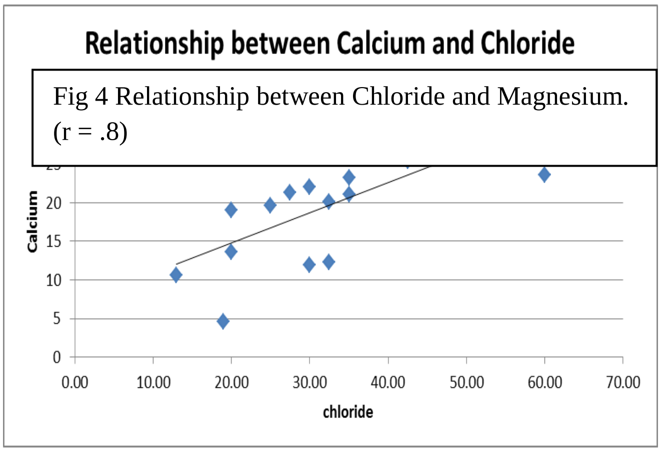


Fig 4 Relationship between Chloride and Magnesium. (r = .8)

Fig. 5 I

(r = .73

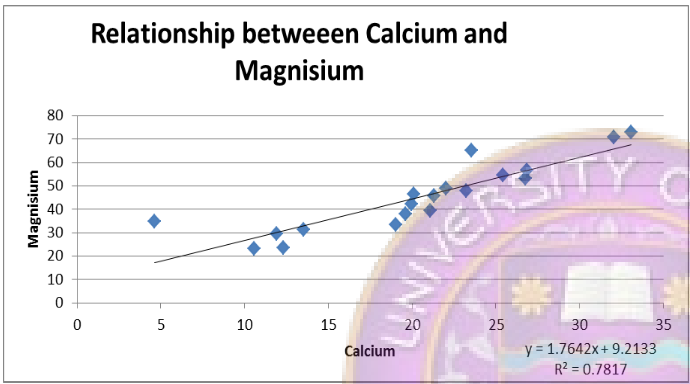


Fig. 6 Relationship between Calcium and Magnisium (r = .88)

Calculated and Designed by Ms Excel - 2010

2. The TDS includes all the salts such as Calcium, Chloride, Magnesium, Fluoride etc. Here the correlation matrix which shown in Table. 2 shows the significantly positive relationship among them which shown in the following scatter diagrams. These scatter diagram are prepared to know how much the points are scattered from the best fit line. The points which are fit on the best fit line having strong correlation and the points which are far from the best fit line indicates the lesser correlation. These all above scatter diagrams show a strong and positive correlation. It means all these salts occurring naturally in this region are due to the high temperature and high electronic conductivity. Because of the high water conductivity in this region the TDS content is also high which leads to increased hardness in water and makes the water unfit for drinking (non-potable), animals and other daily chores.

CONCLUSION

The above study was done with the aim of determining the fluoride levels of the water sources present in the Tehsil Makrana of Nagaur district of Rajasthan. This is the subtopic of the broader area of the research being carried out by the investigators. During the initial surveys conducted, the physical deformities and the health of the residents attracted us to analyse the levels of the fluoride present in the drinking water sources. Besides, the presence of various marble stone mining projects in the areas it also indicates that the water must be laden with high levels of certain salts. On sampling and analysing the water from 19 different villages with the hypothesis that the problems were due to the consumption of high levels of fluoride in this region was proved correct. The drinking water was found to have exceptionally high fluoride and other salts that makes the water non-potable.

There is an emergent need to look for de-fluoridation of the drinking water consumed by the villagers otherwise a large number of persons of working age group would be thrown out of a normal life as is happening in the present scenario.

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