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Research Article

Geochemical Characterisation of Fluoride Containing Groundwater from Sita Nadi Watershed, Bhokar Taluka, Maharashtra, India

Dipak B Panaskar[1*], Vasant M Wagh[2], Ranjeet S Pawar[3]

[1]Department of Science, School of Earth Sciences, SRTM University, Maharashtra, India

[2]Department of Hydrology, School of Earth Sciences, SRTM University, Maharashtra, India

[3]Department of Soil Science, School of Earth Sciences, SRTM University, Maharashtra, India

***Corresponding author:** Dipak B Panaskar, Department of Science, School of Earth Sciences, SRTM University, Maharashtra, India. Tel: +919422188767; Email: dbpanaskar@rediffmail.com

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Abstract

Fluorosis is caused by an excessive ingestion of fluoride through drinking water. The high concentration of fluoride when enters body it causes dental and skeletal fluorosis. Hydrological investigations have been carried out in Bhokar Taluka, Maharashtra. The physicochemical parameters such as pH, EC, TDS, TH, Ca, Mg, Na, K, CO3, HCO3, TA, Cl, SO4 and F have been analysed for pre-and post-monsoon seasons of 2012. In the study area, the fluoride content in groundwater ranges from 0.10 to 6.95 ppm and is seen to be much above the safe limit (1.5 ppm) given by WHO [1]. Mainly groundwater samples from Mahagaon, Divshi khurd, Divshi budruk, Kolgaon khurd, Kolgaon budruk and Matul contain high amount of fluoride. Higher concentration of fluoride is observed in the areas where the granitic rocks are encountered in dug/bore wells. In the study area rock water interaction is the main process which is responsible for the high concentration of fluoride. The fluoride rich minerals must have been dissociated from the rocks and fluoride is dissolved in groundwater by dissolution. In pre-monsoon season the increase of the areal extent of high fluoride concentration (above MPL) and five additional locations showing fluoride concentration above HDL as compare to post monsoon season corroborates the dissolution of fluoride from the basement rocks i.e. granitic rocks through the wall rock interaction process. On the contrary the decrease in the area extent of high fluoride concentration (above MPL) in post monsoon season indicates dilution process due to precipitation. Since the lineament is a weak zone the fluoride from the granitic rock is getting leached out by the process of dissolution and contaminating the groundwater in this region.

Keywords: Bhokar; Fluoride; Geochemistry; Groundwater; India

Introduction

The chemical composition of groundwater is controlled by many factors that include composition of groundwater from precipitation, geological structure and mineralogy of groundwater from the watersheds and aquifers, and geological processes within the aquifer [2]. The interaction of groundwater from all factors leads to various water types. The monitoring of water quality is important for sustainable development and provides valuable information for water management practices. The importance of water quality in human health has recently attracted a great deal of interest. In the developing world, 80% of all diseases are directly related to poor drinking water and unsanitary conditions [3]. Substantial groundwater pollution has resulted from the coupling of agricultural systems demanding large inputs of fertilizers, pesticides, and irrigation water within a physical setting that comprises coarse soils and shallow groundwater [4]. The relation between agricultural practices and groundwater pollution is well established. Groundwater contamination by anthropogenic activities, such as urbanization, industrialization and agricultural activities is a problem in arid and semiarid regions. The quality of groundwater is very important because it is the main factor which decides its suitability for domestic, industrial and agricultural purpose. Hydrogeo chemistry is an essential aspect for better understanding f the suitability of groundwater quality for drinking and irrigation purpose. There are very few and sporadic studies have been carried out in Bhokar area. Now it is well fact that Fluoride is essential for the development of tooth enamel, dentin, and the bones especially to young children below eight years of age when present within permissible limits of 1.0-1.5 mg /l. Excess fluorides in drinking water cause dental fluorosis and skeletal fluorosis. There are few reports of fluorosis appeared in local newspapers. This has prompted the author to undertake present studies with special reference to fluoride contamination. Physico-chemical parameters of groundwater samples from Bhokar watershed were determined and assessed in order to understand the variation of the various parameters and their interrelationship with respect to spatial distribution. Data obtained during the course of both field and laboratory analyses of groundwater samples during the pre-and post-monsoon seasons 2012 have been given in the (Table 1,2). The minimum, maximum, average and standard deviation of the parameters, with locations have been discussed here.

Study Area

For the present study the Sita Nadi Watershed area of Bhokar Taluka, Nanded District has been selected (Figure 1). The study area is bounded by longitude 77°35'and 78°E and latitude 19°'3' and 19°17'N. Geologically, study area is covered by basalt and is underlained by granitic rocks from 4 to 20-meter depth and granite is one of the important natural sources of fluoride contamination. Quartz vein is also intruded between Divshi and Kolgaon villages. The width of quartz vein is about 4 meters, and quartz is one of the important sources for fluoride contamination in water.

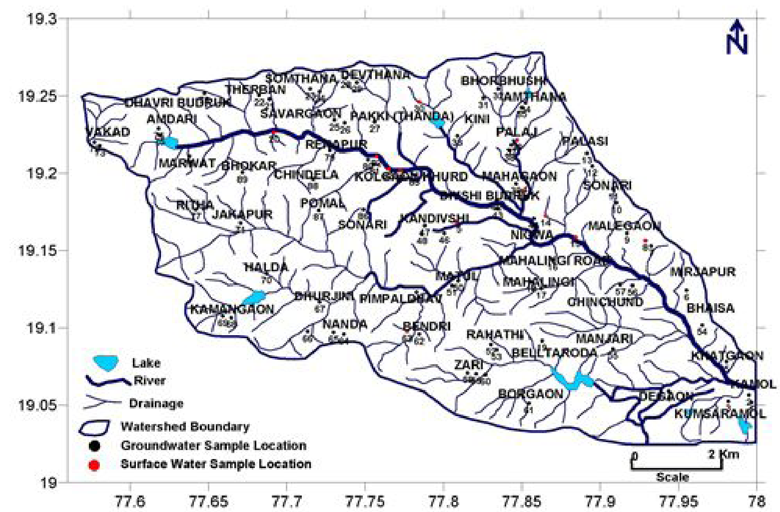

Figure 1: Study Area Map with sample locations.

Material and Methodology

Total 89 representative groundwater samples have been collected for pre-monsoon and post monsoon season 2012. pH and Electrical Conductivity (EC) were measured in the field itself by using portable digital meter. The other physicochemical parameters such as TH, Ca, Mg, TA, CO_3, HCO_3 and Cl were analyzed in the laboratory by following the standard methods of American Public Health Association [5]. The sodium (Na) and potassium (K) ions was determined using flame photometer. The SO_4, PO_4, NO_3 by using spectrophotometer and F were determined by Ion Analyser. Surfer 9.0 software was used for the preparation of spatial distribution map of fluoride.

Results and Discussion

Descriptive statistics of physico-chemical parameters of 89 groundwater samples of pre-monsoon and post monsoon season 2012 in terms of minimum, maximum, average and standard deviation have been given in (Table 1,2) respectively. As mentioned earlier because of very few and sporadic studies have been carried in the study area, detailed geochemical investigations of groundwater have been carried and discussed with spatial and temporal variations.

Spatial and Temporal Variation in the Properties of Groundwater from Bhokar Watershed Aquifers for Pre-monsoon Season 2012 and Post Monsoon Season 2012

The data collected for pre-and post-monsoon seasons 2012 of different parameters have been discussed in relation to spatial and temporal variation and compared with water quality standards given by WHO [1]. The spatial and temporal variation has been assessed with the help of different figures. Data obtained during the course of both field and laboratory analyses of groundwater samples have been discussed as minimum, maximum, average and standard deviation of the parameters, with locations during Pre-and Post-Monsoon Seasons 2012 has been presented in (Table 1,2).

Sr. No.	pH	EC	TDS	TH	Ca	Mg	Na	K	Cl	HCO_3	CO_3	TA	SO_4	F
Min	7.8	620	396.8	70	14.43	3.96	9.5	5.5	26.2	65	0	65	26	0.01
Max	9	6012	3847.7	682	121.84	181.08	388.1	250.1	520.1	330	25	340	128	6.60
Avg	8.51	1752.9	1121.8	285.5	43.77	99.91	86.04	27.72	148.77	180.4	10.1	189.7	66.7	0.82
S.D.	0.29	901.1	576.68	109.95	21.76	41.32	72.79	50.99	102.92	49.6	5.86	51.17	25.38	0.99

Table 1: Descriptive Statistics of Physico-chemical Parameters of Groundwater of Pre-Monsoon Season 2012.

Sr. No.	pH	EC	TDS	TH	Ca	Mg	Na	K	Cl	HCO_3	CO_3	TA	SO_4	F
Min	7.3	598	382.72	38	12.02	3.96	9.8	5.2	32.66	90	0	100	20	0.05
Max	8.9	4687	2999.68	678	155.51	282.19	261	168.9	505.52	630	20	640	118	6.95
Avg	8.15	1507.1	964.55	289.73	52.53	104.62	80.52	20.63	139.0	343.82	7.58	351.40	56.55	0.66
S.D.	0.29	709.96	454.37	147.71	31.75	64.26	65.11	33.46	101.51	103.12	4.53	102.99	22.90	0.96
All values are expressed in mg/l except pH. The Ec are in µS/cm. S.D.= Standard Deviation.														

Table 2: Descriptive Statistics of Physico-chemical Parameters of Groundwater of Post Monsoon Season 2012.

Hydrogen ion Concentration (pH)

pH is relative hydrogen ion concentration in water and it indicates the intensity of acidity or alkalinity. The pH has no direct effect on human health, but change in it alters the taste of water. The pH of groundwater samples varies from 7.8 to 9 in the pre-monsoon season 2012 (Table 1). The minimum pH was recorded from Sample No. 20 and 25, while maximum pH was recorded from the Sample No. 54. The average pH and Standard Deviation of the groundwater is 8.51 and 0.29 respectively. In the post monsoon season 2012, the pH of groundwater samples varies from 7.3 to 8.9 (Table 2). The minimum pH was recorded from Sample No. 47, while maximum pH was recorded from Sample No. 19. The average pH and Standard Deviation of the groundwater is 8.15 and 0.29 respectively. pH values of groundwater for pre-and post-monsoon seasons 2012 have been compared with the maximum desirable limit and maximum permissible limit, given by [1]. It is observed that, the average pH values of groundwater are high in pre-monsoon as compared to post monsoon season. It can be seen that pH has remained alkaline in both the seasons. This can be attributed to the buffering capacity of the aquifer as reflected in total alkalinity values in both the season. In the pre-and post-monsoon seasons 2012 pH values of 100% groundwater samples are above the highest desirable limit, but below maximum permissible limit given by WHO [1] suggesting its suitability for drinking purpose and pH of groundwater does not cause any severe health hazard.

Electrical Conductivity (EC)

Conductivity is the capacity of water to carry an electrical current. This ability depends on the presence of ions, their total concentration, mobility valence, relative concentrations, and on the temperature of measurement. Solutions of most inorganic acids, bases, and salts are relatively good conductors [6]. Conductivity reflects the concentration of dissolved solids in water mainly contributed by inorganic ions. Solids in water mainly refer to suspended or dissolved matter. Solids may affect water or effluent quality adversely in a number of ways. Water with high dissolved solids is not suitable for drinking and may induce physiological reactions in the consumer [7].

Electrical Conductivity of groundwater samples varies from 620 to 6012 µS/cm for pre-monsoon season 2012 (Table 1). The minimum EC was recorded from Sample No. 10, while maximum EC was recorded from Sample No. 41. The average EC and Standard Deviation value of the groundwater is 1752.9 µS/cm and 901.1 respectively. In the post monsoon season 2012, the EC of groundwater samples varies from 598 to 4687 µS/cm (Table 2). The minimum EC was recorded from Sample No. 45, while maximum EC was recorded from Sample No. 72. The average EC and Standard Deviation value of the groundwater is 1507.1 µS/cm and 709.96 respectively.

According to Wilcox [8] classification (Table 3) EC of the majority of the groundwater samples, 75.3% and 76.4% in the pre-and post-monsoon seasons 2012 respectively, of the study area represent permissible water class, while 20.2% and 14.6% of the groundwater samples in the pre-and post monsoon seasons 2012 respectively belong to doubtful water class. Few groundwater samples, 3.4% and 09% in the pre-and post-monsoon seasons 2012 respectively represent good water class. While only one groundwater sample from pre-monsoon season of 2012 falls in unsuitable class.

Range (µS/cm)	Class	Sample Number (%)	
		Pre 12	Post 12
< 250	Excellent	00	00
250-750	Good	03(3.4)	08(9)
750-2250	Permissible	67(75.3)	68(76.4)
2250-5000	Doubtful	18(20.2)	13(14.6)
> 5000	Unsuitable	01(1.1)	00

Table 3: Classification of EC (Wilcox, 1955).

Total Dissolved Solids (TDS)

TDS are composed of carbonates, bicarbonates, chlorides, sulphates, phosphates and nitrates of Ca, Mg, Na, K, and Mn and organic matter, salts and other particles [9]. There is a considerable amount of dilution of concentration of ions during the post monsoon due to precipitation.

TDS of groundwater samples measured during pre-monsoon season of 2012 ranges from 396.8 to 3847.7 mg/l (Table 1). The minimum TDS was recorded from Sample No. 10, while maximum TDS was recorded from Sample No. 41. The average TDS and Standard Deviation value of the groundwater is 1121.8 mg/l and 576.68 respectively. In the post monsoon season 2012, TDS of groundwater samples ranges from 382.72 to 2999.68 mg/l (Table 2). The minimum TDS was recorded from Sample No. 45, while maximum TDS was recorded from Sample No. 72. The average TDS and Standard Deviation value of the groundwater is 964.55 mg/l and 454.37 respectively.

TDS content of majority of the groundwater samples, 80.9% and 86.5% in the pre-and post-monsoon season of 2012 respectively, show low TDS values than maximum desirable limit given by WHO [1] indicating good groundwater for drinking purposes.

Range (mg/l)	Water Class	Sample Number (%)	
		Pre 12	Post 12
< 1000	Fresh	45 (50.6)	56 (62.9)
1000-10000	Brackish	44 (49.4)	33 (37.1)
10000-100000	Saline	00	00
> 100000	Brine	00	00

Table 4: Classification of TDS.

According to the classification of TDS (Table 4) majority of the groundwater samples, 50.6% and 62.9% in the pre-and post-monsoon seasons of 2012 respectively, belong to fresh water class. While 49.4% and 37.1% groundwater samples in the pre-and post-monsoon seasons of 2012 respectively represent brackish water class.

Total Hardness (TH)

Water hardness is an important property, which determines its utility for domestic and industrial activities. Water hardness is a traditional measure of the capacity of water to precipitate soap. Hardness of water is not a specific constituent but is a variable and complex mixture of cations and anions. It is caused by dissolved polyvalent metallic ions. Hardness is a useful water quality indicator. For the most part, however, hardness is a reflection of the amount of calcium and magnesium entering the stream through the weathering of rock such as limestone ($CaCO_3$). When limestone is weathered, it dissolves into calcium (Ca^{2+}) and carbonate (CO_3^{2-}) [2]. The hardness of water reflects the nature of geological formation with which it has been in contact. Water is commonly classified in terms of degree of hardness [10]. The overall interpretation of hydro-chemical analysis in the groundwater samples of Nanded tehsil revelas their slightly alkaline nature and moderately hard to very hard type water [11,12].

Hardness of groundwater samples in the pre-monsoon 2012 varies from 70 to 682 mg/l (Table 1). The minimum TH was recorded from Sample No. 67, while maximum TH was recorded from Sample No. 2. The average Hardness and Standard Deviation value of the groundwater is 285.5 mg/l and 109.95 respectively. In the post monsoon season 2012 the TH of groundwater samples ranges from 38 to 678 mg/l (Table 2). The minimum TH was recorded from Sample No. 67, while maximum TH was recorded from Sample No. 21. The average Hardness and Standard Deviation value of the groundwater is 289.7 mg/l and 147.7 respectively.

TH content of 48.3% and 43.8% in the pre-and post-monsoon season of 2012 respectively show high TH values than maximum permissible limit given by WHO [1] indicating mixing of effluent water in the aquifer and thereby contaminating the groundwater.

According to the classification of TH (Table 5) 48.3% and 42.8% of the groundwater samples in the pre-and post-monsoon season of 2012 respectively falls in very hard water class. 42.8% and 43.8% groundwater samples in the pre-and post-monsoon season of 2012 respectively represent hard water class. While 6.74% and 6.7% groundwater samples in the pre-and post-monsoon season of 2012 respectively belong to moderate water class. Whereas 2.2% and 6.7% groundwater samples in the pre-and post-monsoon season of 2012 respectively represent soft water class. Hardness was slightly increased during post monsoon season; which can be attributed to the leaching content like calcium and magnesium from the soil.

Range (mg/l)	Water Class	Sample Number (%)	
		Pre 12	Post 12
< 75	Soft	02 (2.2)	06 (6.7)

75 - 150	Moderate	06 (6.7)	06 (6.7)
150 - 300	Hard	38 (42.8)	39 (43.8)
> 300	Very Hard	43 (48.3)	38 (42.8)

Table 5: Classification of TH (Sawyer and McCarty, 1967).

Calcium (Ca)

Calcium is one the most abundant element in the natural waters. The quantities in natural waters generally vary from 10 to 100 mg/l depending upon the type of the rocks. Calcium in groundwater is mainly derived from weathering of silicate minerals [13]. Disposal of sewage and industrial waste are also important sources of calcium.

Calcium of groundwater samples varies from 14.43 to 121.84 mg/l in the pre-monsoon season 2012 (Table 1). The minimum Ca was recorded from Sample No. 5, while maximum Ca was recorded from Sample No. 21. The average Calcium and Standard Deviation value of the groundwater is 43.77 mg/l and 21.76 respectively. In the post monsoon season 2012, the Ca of groundwater samples varies from 12.02 to 155.51 mg/l (Table 2). The minimum Ca was recorded from Sample No. 67, while maximum Ca was recorded from Sample No. 21. The average Calcium and Standard Deviation value of the groundwater is 52.53 mg/l and 31.75 respectively.

Ca content of majority of the groundwater samples, 94.4% and 78.7%, in the pre-and post-monsoon season of 2012 respectively, show less Ca values than desirable limit given by WHO [1] indicating groundwater is good for drinking purposes.

According to the WHO [1] drinking water standards of Ca content of 94.4% and 78.7% groundwater samples in the pre-and post-monsoon season of 2012 respectively falls below the desirable limit. While 5.6% and 21.3% groundwater samples in the pre-and post-monsoon season of 2012 respectively falls above highest desirable limit but below the maximum permissible limit.

Magnesium (Mg)

Magnesium also occurs in all kinds of natural waters with calcium, but its concentration remains generally lower than the calcium. The principal sources in the natural waters are various kinds of rocks. Sewage and industrial wastes are also important contributors of magnesium. Similar to calcium, the concentration of magnesium also depends upon exchange equilibiria and presence of the ions like sodium. Natural softening of water occurs during percolation through soil by exchange with sodium ions. It is supposed to be non-toxic but high concentration combined with sulphate acts as laxative to human beings. One of the sources of magnesium in groundwater is rock [14].

Magnesium arises principally from the weathering of rocks containing ferromagnesium minerals and from some carbonate rocks. Mg occurs in many organometallic compounds and in organic matter, since it is an essential element for living organisms [15]. The high magnesium content results increase soil salinity, and adverse effects on crop yield in groundwaters of Nanded tehsil [16]. Magnesium of groundwater samples in the pre-monsoon season of 2012 ranges from 3.96 to 181.08 mg/l (Table 1). The minimum Mg was recorded from Sample No. 69, while maximum Mg was recorded from Sample No. 83. The average Magnesium and Standard Deviation value of the groundwater is 99.91 mg/l and 41.32 respectively. In the post monsoon season 2012, the Mg of groundwater samples ranges from 3.96 to 282.19 mg/l (Table 2). The minimum Mg was recorded from Sample No. 41, while maximum Mg was recorded from Sample No. 73. The average Magnesium and Standard Deviation value of the groundwater is 104.62 mg/l and 64.26 respectively. Mg content of majority of the groundwater samples, 49.4% and 47.2%, in the pre-and post-monsoon season of 2012 respectively, show High Mg values than maximum permissible limit given by WHO [1] indicating groundwater is not safe for drinking purposes.

Sodium (Na)

All-natural waters contain some sodium since sodium salts are highly water-soluble and sodium is one of the most abundant elements on earth. Concentrations of sodium in natural water vary considerably depending on local geological conditions and wastewater discharges [15]. The levels of sodium may vary from less than 1 mg/l to more than 500 mg/l, relatively high concentration may be found in brines and hard waters softened by the sodium exchange process. The ratio of sodium to total cations is important in agriculture and human pathology. Soil permeability can be harmed by a high sodium ratio. Persons affected with certain diseases require water with low sodium concentration [2]. There are no health based drinking water standards for sodium and potassium. Sodium salts are natural constituents of ground water because of the abundance of evaporite minerals in the earth's crust.

Sodium of groundwater samples in the pre-monsoon season of 2012 ranges from 9.5 to 388.1 mg/l (Table 1). The minimum Na was recorded from Sample No. 56, while maximum Na was recorded from Sample No. 41. The average sodium and Standard Deviation value of the groundwater is 86.04 mg/l and 72.79 respectively. In the post monsoon season 2012, the Na of groundwater samples ranges from 9.8 to 261 mg/l (Table 2). The minimum Na was recorded from Sample No. 66, while maximum Na was recorded from Sample No. 41. The average sodium and Standard Deviation value of the groundwater is 80.52 mg/l and 65.11 respectively. Na content of majority of the groundwater samples, 88.8% and 92.1%, in the pre-and post-monsoon season of 2012 respectively, show Less Na content than the highest desirable limit while 11.2% and 7.9% groundwater samples in the pre-and post-monsoon season of 2012 respectively falls above the highest desirable limit given by WHO [1].

Potassium (K)

Potassium is naturally occurring element; however, the concentrations remain quite lower than the sodium, calcium, and magnesium. The major source of potassium in natural waters is weathering of the rocks but the quantities increases in the polluted waters due to disposal of waste water. It has a similar chemistry like sodium and remains mostly in solution without undergoing any precipitation. It also enters the exchange equilibria of the adsorbed cations. As such, it is not very much significant from the health point of view, but large quantities may be laxative [14]. The concentration of potassium in most drinking waters seldom reaches 20 mg/l. However, occasional brines may contain more than 100 mg/l [2].

Potassium of groundwater samples in the pre-monsoon season of 2012 ranges from 5.5 to 250.1 mg/l (Table 1). The minimum K was recorded from Sample No. 77, while maximum K was recorded from Sample No. 23. The average potassium and Standard Deviation value of the groundwater is 27.72 mg/l and 50.99 respectively. In the post monsoon season 2012, the K of groundwater samples ranges from 5.2 to 168.9 mg/l (Table 2). The minimum K was recorded from Sample No. 2 and 77, while maximum K was recorded from Sample No. 49. The average potassium and Standard Deviation value of the groundwater is 20.63 mg/l and 33.46 respectively.

Chloride (Cl)

Chlorides occur naturally in surface and groundwater. The main sources of chlorides are atmospheric precipitation, sedimentary rocks, domestic and industrial sewages. The presence of chloride in natural waters can be attributed to dissolution of salt deposits, seawater intrusion in coastal areas, Sewage effluent and many industrial wastes contain appreciable amounts of chlorides. Each of these sources may result in local contamination of both surface water and groundwater. The chloride content normally increases as the mineral content increases. Upland and mountain supplies usually are quite low in chlorides, whereas river and groundwater usually have a considerable amount. Human excreta, particularly the urine, contain chloride in an amount about equal to the chlorides consumed with food and water. This amount averages about 6 grams of chloride per person per day [10].

Chloride of groundwater samples in the pre-monsoon season of 2012 varies from 26.2 to 520.1 mg/l (Table 1). The minimum chloride was recorded from Sample No. 52, while maximum chloride was recorded from the Sample No. 41. The average chloride and Standard Deviation value of the groundwater is 148.77 mg/l and 102.92 respectively. In the post monsoon season 2012 Chloride of groundwater samples ranges from 32.66 to 505.52 mg/l (Table 2). The minimum chloride was recorded from Sample No. 53 while maximum chloride was recorded from Sample No. 39. The average chloride and Standard Deviation value of the groundwater is 139 mg/l and 101.5 respectively.

Chloride content of majority of the groundwater samples, 73% and 73% in the pre-and post-monsoon season of 2012 respectively, show Less Cl content than the highest desirable limit. While 27% and 27% of the groundwater samples in the pre-and post-monsoon season of 2012 respectively show its contents above the highest desirable limit given by WHO [1] indicating mixing of effluent water in the aquifer and there by contaminating the groundwater.

Alkalinity, Bicarbonates and Carbonates (TA, HCO_3 and CO_3)

The alkalinity of natural waters is due to the salts of carbonates, bicarbonates, borates, silicates and phosphates along with the hydroxyl ions in the Free State. However, the major portion of the alkalinity in natural waters is caused by hydroxide, carbonate and bicarbonate, which may be ranked in order of their association with high pH values. Alkalinity in excess of alkaline earth metal concentration is significant in determining the suitability of water for irrigation [2].

Alkalinity of natural waters is its quantitative capacity to neutralize strong acid to a designated pH. An even neutral water sample shows considerable alkalinity, because it is a capacity function, different from intensity function [17]. Carbonate, bicarbonate and hydroxide salts of calcium, magnesium and other elements contribute for the total alkalinity of groundwater samples.

Carbonate (CO3)

Carbonate of groundwater samples in the pre-monsoon season of 2012 varies from 0 to 25 mg/l (Table 1). The minimum Carbonate was recorded from Sample No. 19, 20, 21, 22, 25, 27, 34, 63, 67, 85 and 88, while maximum Carbonate was recorded from Sample No. 16 and 43. The average Carbonate and Standard Deviation value of the groundwater is 10.1 mg/l and 5.86 respectively. In the post monsoon season 2012 Carbonate of groundwater samples ranges from 0 to 20 mg/l (Table 2). The minimum Carbonate was recorded from Sample No. 06, 14, 20, 24, 29, 34, 64, 68, 77, 82, 83 and 89, while maximum Carbonate was recorded from Sample No. 17 and 53. The average Carbonate and Standard Deviation value of the groundwater is 7.58 mg/l and 4.53 respectively.

Bicarbonates (HCO_3)

Bicarbonate of groundwater samples in the pre-monsoon season of 2012 varies from 65 to 330 mg/l (Table 1). The minimum

Bicarbonate was recorded from Sample No. 85, while maximum Bicarbonate was recorded from Sample No. 83. The average Bicarbonate and Standard Deviation value of the groundwater is 180.4 mg/l and 49.6 respectively. In the post monsoon season 2012 Bicarbonate of groundwater samples ranges from 90 to 630 mg/l (Table 2). The minimum Bicarbonate was recorded from Sample No. 41 and 85, while maximum Bicarbonate was recorded from Sample No. 39. The average Bicarbonate and Standard Deviation value of the groundwater is 343.8 mg/l and 103.1 respectively.

Total Alkalinity (TA)

Alkalinity of groundwater samples in the pre-monsoon season of 2012 varies from 65 to 340 mg/l (Table 1). The minimum alkalinity was recorded from Sample No. 85, while maximum alkalinity was recorded from Sample No. 83. The average total alkalinity and Standard Deviation value of the groundwater is 189.7 mg/l and 51.17 respectively. In the post monsoon season 2012 Alkalinity of groundwater samples ranges from 100 to 640 mg/l (Table 2). The minimum alkalinity was recorded from Sample No. 85, while maximum alkalinity was recorded from Sample No. 39. The average total alkalinity and Standard Deviation value of the groundwater is 351.4 mg/l and 103 respectively.

Sulphate (SO_4)

Sulphate is found naturally in various minerals. It is used in various chemical industries. It is the important anion in groundwater. It reaches to groundwater from industrial waste, atmospheric deposition and natural mineral sources such as gypsum and oxidation of pyrites [18].

Sulphate ions usually occur in natural waters. Many sulphate compounds are readily soluble in water. Most of them originate from the oxidation of sulphide ores, the solution of gypsum and anhydrite, the presence of shales, particularly those rich in organic compounds, and the existence of industrial wastes. Sulphur-bearing minerals are common in most sedimentary rocks. In the weathering process gypsum (calcium sulphate) is dissolved and sulphide minerals are partly oxidised, giving rise to a soluble form of sulphate that is carried away by water. In humid region, sulphate is readily leached from the zone of weathering by infiltrating waters and surface run off but in semiarid and arid regions the soluble salts may accumulate within a few tens of feet of land surface. Where this occurs, sulphate concentration in shallow groundwater may exceed 5000 mg/l and gradually decrease with depth. Sulphate has highest values in summer because of high organic pollution and reduced water flow. According to Pawar and Shaikh [19] sulphate enters into groundwater due to percolation of sulphate containing fertilizers. According to Karanth [13] rock is one of the sources of sulphate in groundwater and source of sulphate in rocks are sulphur minerals, sulphides of heavy metals, which is commonly occurred in igneous and metamorphic rocks. Apart from natural source there are some anthropogenic sources like application of sulphate fertilizers.

Sulphate of groundwater samples varies from 26 to 128 mg/l for pre-monsoon season of 2012 (Table 1). The minimum SO_4 was recorded from Sample No. 67, while maximum SO_4 was recorded from Sample No. 28 and 81. The average sulphate and Standard Deviation value of the groundwater is 66.7 mg/l and 25.38 respectively. In the post monsoon season 2012, the SO_4 of groundwater samples varies from 20 to 118 mg/l (Table 2). The minimum SO_4 was recorded from Sample No. 20, while maximum SO_4 was recorded from Sample No. 28. The average sulphate and Standard Deviation value of the groundwater is 56.6 mg/l and 22.9 respectively.

Fluoride (F)

Environmental fluorine enrichment has both natural and anthropogenic sources. Chemical weathering of some fluoride containing minerals leads to fluorine enrichment of soils and groundwater [20]. Discharge of fluoride from some industries, e.g. semiconductors, steel, aluminum, glass, ceramic factories, phosphate fertilizers and electroplating are among the main anthropogenic sources of fluoride pollution [21]. Extensive application of phosphate fertilizers (containing 1.5% to 4% F) in agriculture is another important source of fluoride input to soils [22]. Interaction of fluoride with soil plays an important role in determining F transport and bioavailability. Sorption of fluoride on soils is closely related to the constituents of soil clays, solution pH, and Al F complexation [23,24]. The element is mainly stored in clay soils, groundwater and lakes in volcanic areas. Groundwater is the most important source of fluoride. Secondary sources are related to pollution from industries (ceramic factories, coal burning) and agricultural activities, particularly the use of phosphatic fertilizers.

According to Perl man [25] fluorite is the most widely distributed fluorine-bearing mineral in nature while fluorapatite is a very common member of the immiscible phase generated during early differentiation of mafic and ultramafic magmas, forming apatite-magnetite rocks. Under supergene environment, on account of its high reactivity coefficient, the element occurs as highly mobile fluoride ion, but its mobility is severely restricted across a calcium barrier due to CaF2 precipitation [25]. It is for this reason that, under supergene environment, the average fluorine content of calcium rich sedimentary rocks, like calcareous shale, limestones, dolomite, calcareous sandstone etc. is high [26].

According to Koritnig [27] during weathering in humid tropical/subtropical climates the geochemical fate of fluorine is controlled by series of intricate processes, involving adsorption-desorption reactions and dissolution - precipitation reactions. During weathering of granite massifs, fluorine is leached out in the initial stage itself. The fluorine in apatite is very stable, while fluorine from mica is leached out rapidly. Fluorite (CaF2), if present, is dissolved slowly by the circulating water. It is reported that in soil profile decreasing fluorine content with increasing distance from the parent rock [28]. It is also observed that, under acidic circulating solution, fluorine is readily absorbed in clay structure, while in alkaline environment it is desorbed. During natural hydration and diversification of glassy rocks and glasses, about half of the original fluorine present is solubilised, leached and lost, through fluorine adsorption by hydrated and devitrified glass from coexisting ground water [29]. In general, abundance of fluorine in fresh water varies between 0.25 to 1 ppm [30]. Many workers [31] determined fluoride content of surface water and it ranges from 0 to 6.4 mg/l. During weathering and circulation of water in rocks and soils, fluorine can be leached out and dissolved in ground water. The fluorine content of groundwater varies greatly (0 to 35) mg/l depending on the types of rocks from which they originate [32,33]. In arid and semi-arid regions, the fluoride content of ground water is higher, compared to groundwater from humid areas. This is probably due to higher TDS in groundwater, resulting in increased ionic strength and consequently higher CaF2 solubility in the groundwater. In such cases, viscosity of the ground water would tend to increase and consequently, the yield of the wells would decrease [34].

Fluorine is a necessary micronutrient for both humans and animals. Fluorine occurs as F in soils and natural waters [24]. A concentration of fluoride in drinking water in the range of 0.5-1.0 mg/l is beneficial for the production and maintenance of healthy bone and teeth. The acceptable maximum concentration of fluoride in drinking water is 1.5 mg/l [35-38]. Fluoride is essential for the development of tooth enamel, dentin, and the bones. As several studies have shown, low doses of fluoride are useful for the prophylaxis of caries, and for the treatment of osteoporosis [39]. Fluoride is beneficial especially to young children below eight years of age when present within permissible limits of 1.0-1.5 mg /l for calcification of dental enamel. Excess fluorides in drinking water cause dental fluorosis and skeletal fluorosis [40]. It is evident from the information available that a certain quantity of fluorine is essential for the formation of caries-resistant dental enamel and for the normal process of mineralization in hard tissues. The element is metabolized from both electrovalent and covalent compounds. Low fluoride concentrations stabilize the skeletal systems by increasing the size of the apatite crystals and reducing their solubility. About 95% of the fluoride in the body is deposited in hard tissues and it continues to be deposited in calcified structures even after other bone constituents (Ca, P, Mg and CO_3) have reached a steady state. Age is an important factor in deciding to what extent fluorine is incorporated into the skeleton. The uptake almost ceases in dental enamel after the age of about 30 years. Fluorine render more resistance to acid dissolution, it inhibits bacterial enzyme system, reduce tendency of enamel to absorb proteins, reduce depth of pits.

Effects of Fluoride on Human beings

Excessive fluoride exposure through drinking water is the prime causative factor in development of fluorosis [41]. Calcium ions bind fluoride and critically lower its bioavailability [25,42,43]. Fluorosis commonly affects undernourished, tribal and rural population groups in the underdeveloped and developed countries, lying between 150 300 latitudes on both the sides of equator [44].

Dental Fluorosis

Due to excessive fluoride intake, enamel loses its luster. In its mild form, dental fluorosis is characterized by white, opaque areas on the tooth surface and in severe form; it is manifested as yellowish brown to black stains and severe pitting of the teeth. This discoloration may be in the form of spots or horizontal streaks [45]. Normally, the degree of dental fluorosis depends on the amount of fluoride exposure up to the age of 8-10 years, as fluoride stains only the developing teeth while they are being formed in the jawbones and is still under the gums. The effect of dental fluorosis may not be apparent if the teeth are already fully grown prior to the fluoride over exposure. Therefore, the fact that an adult shows no signs of dental fluorosis does not necessarily mean that his or her fluoride intake is within the safety limit. Long-term consumption of water containing fluoride 1 mg/l leads to dental fluorosis. White and yellow glistening patches on the teeth are seen which may eventually turn brown. The yellow and white patches then turned brown horizontal streaks. The brown streaks may turn black and affect the whole tooth and may get pitted, perforated and chipped off at the final stage. Dental fluorosis not only poses cosmetic problems but has serious social problems too, in terms of matrimonial problems of the children. The intensity of fluorosis is not merely dependent on the fluoride content in water, but also on the fluoride from other sources, physical activity and dietary habits [46,47]. Excessive intake may result in slow, progressive crippling scourge known as fluorosis. There are more than 20 developed and developing nations that are endemic for fluorosis and although the relationship between fluoride and tooth decay is complex, and not yet fully understood [48,49]. The two principle factors influencing dental caries are diet and the use of fluoridated dental care products (especially toothpaste). Dental fluorosis is a form of developmental defect of tooth enamel. Histologically it presents as a hypo calcification, while clinically it ranges from barely visible white striations on the teeth through to gross defects and staining of the enamel [50]. There are around 90 different causes of enamel defects, of which three or four causes are common. Minor forms of dental fluorosis are not aesthetically troublesome and may even enhance the appearance of dental enamel [51].

Skeletal Fluorosis

The symptoms of skeletal fluorosis have been observed in persons when water contains more than 3 to 6 mg/l of fluoride. Skeletal fluorosis affects young and old alike. Fluoride can also damage the fetus if the mother consumes water and food, with a high concentration of fluoride during pregnancy, infant mortality due to calcification of blood vessels can also occur [52]. Skeletal fluorosis does not easily manifest until the disease attains an advanced stage. Fluoride mainly gets deposited in the joints of neck, knee, pelvic and shoulder bones and makes it difficult to move or walk [53]. Some of the symptoms of skeletal fluorosis are severe pain in the backbone, Stiffness of the backbone, Severe pains in the joints, Severe pains in the hip region, Immobile / Stiff joints, Increased densities of bones, besides calcification of ligaments, Construction of vertebral canal and intervertebral foramen-pressure on nerves and Paralyses.

Fluoride of groundwater samples in the pre-monsoon season of 2012 ranges from 0.01 to 6.6 mg/l (Table 1). The minimum Fluoride was recorded from Sample No. 69 while maximum Fluoride was recorded from Sample No. 39. The average Fluoride and Standard Deviation value of the groundwater is 0.82 mg/l and 0.99 respectively. In the post monsoon season 2012, the Fluoride of groundwater samples ranges from 0 to 6.95 mg/l (Table 2). The minimum Fluoride was recorded from Sample No. 30, while maximum Fluoride was recorded from Sample No. 39. The average Fluoride and Standard Deviation value of the groundwater is 0.66 mg/l 0.96 respectively.

Highest desirable limit of F is 1 mg/l and maximum permissible limit is 1.5 mg/l given by WHO [1]. Fluoride content of majority of the groundwater samples (75.3% and 91%) in the pre-and post-monsoon season of 2012 respectively show Less F content than the highest desirable limit (Figure 2). 11.2% and 1.1% of the groundwater samples in the pre-and post-monsoon season of 2012 respectively falls above the highest desirable limit, but below the Maximum permissible limit. While 13.5% and 7.9% of the groundwater samples in the pre-and post-monsoon season of 2012 respectively of the study area are falls in above the Maximum permissible limit given by WHO [1].

It is evident from the figure 3 that high fluoride concentration (above Maximum Permissible Limit (MPL)) areas are located at center of the Sita river watershed while fluoride concentration above Highest Desirable Limit (HDL) but below Maximum permissible limit areas are located at the center as well at five different locations on the southern part of the Sita river watershed in the pre-monsoon season of 2012. While it is apparent from the figure 4 that high fluoride concentration (above Maximum permissible limit) areas are located at center of the Sita river watershed. In pre-monsoon season the increase of the areal extent of high fluoride concentration (above MPL) and five additional locations showing fluoride concentration above HDL (Figure 3) as compare to post monsoon season (Figure 4) corroborates the dissolution of fluoride from the basement rocks i. e. granitic rocks through the wall rock interaction process. On the contrary the decrease in the areal extent of high fluoride concentration (above MPL) in post monsoon season indicates dilution process due to precipitation (Figure 4).

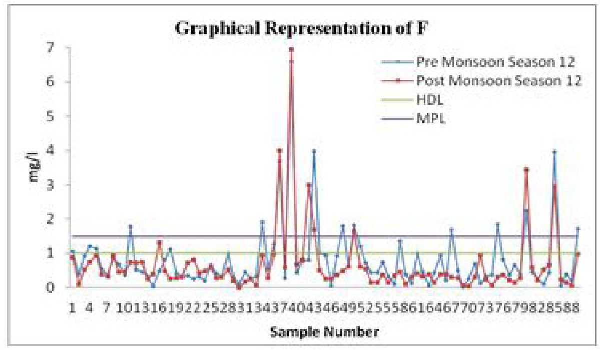

Figure 2: Spatial and Temporal Variation of F of Groundwater in the Study Area.

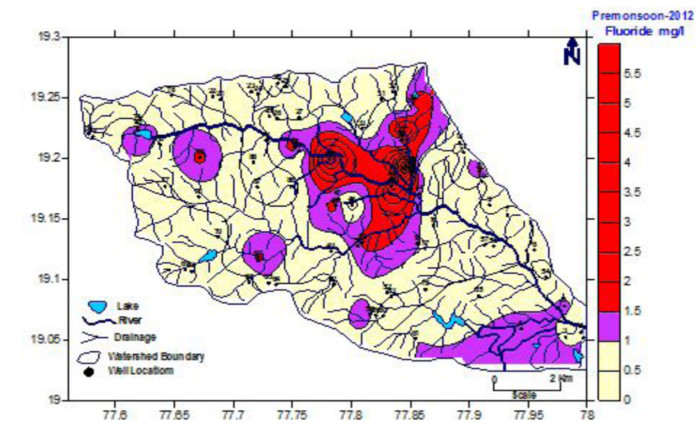

Figure 3: Spatial distribution of Fluoride in Groundwater of the Study Area.

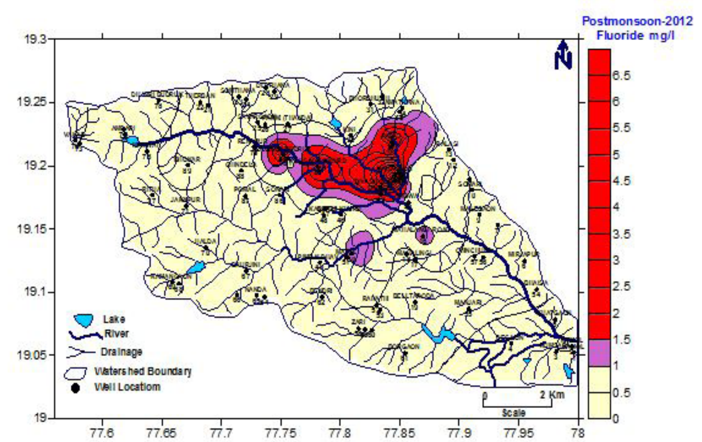

Figure 4: Spatial distribution of Fluoride in Groundwater of the Study Area.

Mainly groundwater samples from Mahagaon, Divshi khurd, Divshi budruk, Kolgaon khurd, Kolgaon budruk and Matul contain high amount of fluoride. Majority of study area is covered by basalt and is underlained by granitic rocks. The granite is one of the important sources of fluoride contamination. Most of the groundwater samples from study area show fluoride concentration below permissible limit, but on the other hand people from such areas are also affected by dental fluorosis, it indicates that water is not only the source of fluoride contamination other factors like nutrition and environmental condition are also responsible.

It is revealed that the main factors responsible for increase in fluoride concentration are geological, chemical and physical characteristics of the aquifer, the porosity of the soil and rocks, rock water interaction, rainfall, and temperature.

The higher values of fluoride in groundwater can be attributed to dissolution of fluoride from natural sources like granitic rocks, mica and other fluoride bearing minerals present in study area and anthropogenic activities like application of phosphate fertilizers because study area has intensive agricultural belt and farmers are using lot of phosphate fertilizers. Majority of study area is covered by basalt and is underlined by granitic rocks from 4 to 20-meter depth and granite is one of the important natural sources of fluoride contamination. Quartz vein is also intruded between Divshi and Kolgaon villages. The width of quartz vein is about 4 meters, and quartz is one of the important sources for fluoride contamination in water.

It is seen that the major trend of the lineaments NW- SE and NE- SW. The major lineaments trend in the NW- SE direction while the minor lineaments trend in the NE- SW direction. The one major lineament i.e. Sita lineament trending in NW- SE direction which follows the Sita River course and passes from Renapur, Kolgaon budruk, Kolgaon khurd, Divshi budruk and Divshi khurd villages [54]. It is interesting to note that the groundwater samples which are in the vicinity of Sita lineament show more concentration of fluoride. This can be attributed to the granitic rocks as a source of fluoride which is overlained by basalt in this area. Since the lineament is a weak zone the fluoride from the granitic rock is getting leached out by the process of dissolution and contaminating the groundwater in this region.

Conclusions

In pre-monsoon season the increase of the areal extent of high fluoride concentration (above MPL) and five additional locations showing fluoride concentration above HDL as compare to post monsoon season corroborates the dissolution of fluoride from the basement rocks i. e. granitic rocks through the wall rock interaction process. On the contrary the decrease in the area extent of high fluoride concentration (above MPL) in post monsoon season indicates dilution process due to precipitation. Since the lineament is a weak zone the fluoride from the granitic rock is getting leached out by the process of dissolution and contaminating the groundwater in this region.

In most of the water samples the concentration of fluoride was increased in pre-monsoon season than post monsoon season, it can be attributed to weathered geological formations which may be the main source of fluoride in groundwater and availability of fluoride bearing minerals and sufficient contact period for dissolution of fluoride. The concentration of fluoride in groundwater during the post monsoon season were generally less than pre-monsoon season because of dilution by rain water. In some of the water samples the concentration of fluoride was increased in post monsoon season than pre-monsoon season it may be due to the leaching of fluoride due to precipitation from anthropogenic sources like phosphate fertilizers used in agricultural practices.

The fluoride is unevenly distributed in groundwater and its concentration keeps on changing with time to time both vertically and horizontally. Hence every drinking water source has to be tested individually and regular monitoring has to be done and the high fluoride well should be banned for the usage for drinking as well as irrigation purpose.

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