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Assessment of Groundwater Quality With Respect to Fluoride

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Abstract

Groundwater is the major source of drinking water and dietary fluoride in human beings in rural as well as urban areas throughout the world. The objective of the present investigation was to determine the fluoride and other water quality parameters in the ground water of Dabwali town of Sirsa district of Haryana, India. A total of fifty two groundwater samples were randomly collected at different depths from tube wells and hand pumps. The fluoride content in underground water is determined by SPADANS method. From the study it was observed that Dabwali is highly fluoride endemic area. The results showed that fluoride concentration in the ground water of Dabwali ranges from 0.90-34.50 mg/l with a mean of 2.20 ± 18.13 mg/l. Mostly people use groundwater for domestic and irrigation purpose. Therefore, the intake of fluoride concentration is very high as people using groundwater without any prior treatment. The results suggest that the groundwater should be used by the residents only after defluoridation.

Keywords: Defluoridation, Fluoride, Fluorosis, Groundwater, Nitrate, Water Quality.

1. Introduction

Groundwater is the major source of drinking water and dietary fluoride in human beings in rural as well as urban areas throughout the world. Fluoride ion in drinking water is known for both beneficial and detrimental effects on health. It is essential for normal mineralization of bones and formation of dental enamel with presence in small quantity (Chouhan and Flora, 2010) When fluoride is taken up more than the permissible limit, it becomes toxic and causes clinical and metabolic disturbances in animals and human beings such as dental and skeletal fluorosis (Singh *et al*., 2007).The amount of fluoride present naturally in groundwater is governed principally by climate, composition of the host rock and hydrogeology (Gupta *et al*.,2006) Some anthropogenic activities are also contributed to cause an increase in fluoride concentration in groundwater such as use of phosphatic fertilizers, pesticides and sewage and sludges, depletion of groundwater table etc (Ramanaiah *et al*. 2006). Hence to monitor the groundwater quality a lot of studies carried out through-out the world nowadays (Nagarajan *et al*. 2010; Gautam *et al*. 2011 and Kumar, 2011).

Fluoride is considered as a major pollutant of ground water on global scale. Nearly 25 countries in the world are suffering from excess of fluoride content in the groundwater and India is one of them. Periodic incidences of high fluoride content in ground water have been reported in various states of India. Approximately 20 states of India are facing the problem of excessive fluoride in the ground water and about 62 million people including 6 million children suffer from fluorosis because of consumption of water with high fluoride concentrations (UNICEF, 1999). According to WHO (1997) the permissible limit for fluoride in drinking water is 1.5 mg/l, whereas, USPHS (1962) has set a range of allowable concentrations for fluoride in drinking water for a region depending on its climatic conditions because the amount of water consumed and consequently the amount of fluoride ingested being influenced primarily by the air temperature (Singh *et al*., 2007). The major sources of fluoride in groundwater are fluoride-bearing rocks such as fluorspar, cryolite, fluorapatite and hydroxylapatite (Agarwal *et al*., 1997). Fluoride ions from these minerals leach into the groundwater and contribute to high fluoride concentrations (Latha *et al*., 1999; Ramesam and Rajagopalan 1985).

Dabwali in district Sirsa, Haryana is one of the most intensively cultivated areas, high fertilizers and pesticides using area with alarming rate of depletion of groundwater table. A bibliographic survey also reveals that no studies have been undertaken in Dabwali for assessment of fluoride concentration in its groundwater. The present study was, therefore, undertaken to investigate the high concentration of fluoride in groundwater of Mandi Dabwali-district Sirsa of Haryana, India.

2. Materials and Methods

2.1 Study area

Dabwali is a city and a municipal committee in Sirsa district of Haryana, India. It is located on the border of Haryana and Punjab and is just a few minutes travel from Rajasthan border. A total of 52 samples of ground water were collected from different locations of the Dabwali town. In Dabwali town, groundwater is the only source of drinking water. The water is extracted using hand pumps and tube wells. Geological formations vary from loamy sand to sandy loam, with some sandy soils occurring in patches. The soil texture in the belt along Ghaggar River varies from silt-loam to silty- clay loam. The climate of the area is characterized by its dryness, extremes of temperature and scanty rainfall. The mean daily maximum temperature during May and June, which is the hottest period, varies from 41 to 46 °C. The average annual rainfall is varies from 100 to 400 mm.

2.2. Water sampling

A total of 52 samples of ground water were collected from the different locations of town from hand pumps and tube wells after flushing for about 10 minutes on March, 2007. The samples were collected in precleaned, sterilized and polyethylene bottles. The analysis was carried out as per the standard methods mentioned in APHA (1995). pH, electrical conductivity, total dissolved salts, total alkalinity, total hardness, calcium, magnesium, chloride, nitrate and fluoride content was estimated from the collected groundwater samples.

2.3. Reagents and standards

All the reagents used in the present study were of analytical grade (AR) and double distilled water was used through-out the study. Sodium fluoride is used for preparing standard solutions in the range of 1-1.4 mg/l.

2.4. Methodology

The pH of samples was determined by using a pH meter (Systronics, 335) based on Wheatstone bridge principle. The electrical conductivity (EC) of the water samples was estimated by using 'Systronic Conductivity Meter 304'.Total dissolved solids were calculated using the formula suggested by United States Salinity Laboratory Staff (1954). The total hardness, calcium and magnesium were determined by Ethylene diamine tetra acetic acid (EDTA) titration method and total alkalinity was determined by standard sulphuric acid titration method. Chloride was determined by argentometric titration. Fluoride in water samples was determined by SPADANS–zirconyl oxychloride method using UV–VIS spectrophotometer (systronics-118). The absorbance values obtained at λ max equal to 570 nm were compared with the standard calibration curve for fluoride concentration. The nitrate content was estimated by brucine sulphate method using UV–VIS spectrophotometer (systronics-118) at 410 nm. All the experiments were carried out in triplicate and mean value of each sample was considered as the final reading. Statistical analysis was carried out by using SPSS (Statistical Package for Social Sciences).

3. Results and Discussion

The groundwater had no color, odor and turbidity. The taste of groundwater was slightly salty at most of the locations. Table-1 shows a comparison of groundwater quality of the area under study with drinking water standards (ISI, 1993 and WHO, 1997).
The data revealed considerable variations in the water samples with respect to chemical composition

3.1 pH

pH indicates the intensity of acidity or alkalinity and measures the hydrogen ion concentration in water. Though pH has no direct effect on human health but all the biochemical reactions are sensitive to variation in pH. For most of the reactions as well as for human beings, pH seven of drinking water is considered as the best and ideal. The ground water was slightly alkaline ranging from 7.20 to 8.10 but these values were within WHO and ISI permissible limit.

Table-1: Statistical Analysis and Comparison of Groundwater of Mandi Dabwali with Drinking Water Standards

Parameters	Range of Samples				ISI Standards(India,1993)		WHO Limit
	Min.	Max.	Mean	S.D.	Accept. Limit	Max. Limit	
pH	7.20	8.10	7.60	±0.43	7.0-8.5	6.5-9.2	8.0-8.5
EC	0.20	4.00	1.91	±1.09	-	-	-
TDS	128	2560	1222.40	±16.82	500	1500	500
TA	300	790	526.50	±13.90	200	600	-
TH	116	518	290.40	±11.13	200	600	100
Na^+	52.0	440.8	255.62	±41.44	50	-	-
K^+	1.00	90.0	17.10	±15.84	-	-	-
Ca^{2+}	21.2	66.6	56.40	±13.98	75	200	75
Mg^{2+}	29.22	123.40	119.30	±35.00	200	400	50
CO_3^{2-}	0.00	0.00	0.00	±0.00	75	200	75
HCO_3^-	300.2	955.70	161.06	±22.59	30	-	150
Cl^-	70.2	295.30	168.03	±12.57	200	1000	200
NO_3^-	0.00	48.50	6.74	±14.94	200	400	200
PO_4^{3-}	0.00	0.40	0.07	±0.15	-	-	-
F^-	0.90	34.50	2.20	±18.13	1	1.5	1

Values are expressed in mg/l except pH while EC is expressed in mS.

3.2 Electrical Conductivity (EC) and Total Dissolved Salts (TDS)

Electrical conductivity signifies the amount of total dissolved salts, which in turn indicates the inorganic pollution load of the water. TDS further indicates the salinity behavior of ground water. According to WHO, the maximum acceptable concentration of TDS in groundwater for domestic purposes is 500 mg/L and excessive permissible limit is 1500 mg/L. There was a large variation in EC. The EC varied from 0.20 to 4.00 milliSemens (mS). The average value of EC was 1.91 ± 1.09 mS and TDS was 1222.40 ± 16.82 mg/l. According to Rabinove (1958) the ground water was slightly saline at 32 locations covering Bus Stand, Anaj Mandi and Chautala Road etc while rest of 20 samples was non saline.

3.3 Total Hardness, Calcium and Magnesium

Total hardness is an important parameter of water for its use in domestic sector. If hard water is used for longer period, it may be one of the main causes of kidney stone formation in human body. At domestic level if hard water is used for washing, cause wastage of soap. In groundwater, hardness is mainly due to carbonates, bicarbonates, sulphates and chlorides of calcium and magnesium. Hardness in the ground water of Dabwali town ranged from 116 to 518 mg/l with a mean of 290.40 ± 11.13 mg/l. According to classification of total hardness by Durfor and Becker (1964) the ground water of Mandi Dabwali was moderately hard at 13 locations and very hard at 39 locations.The calcium content in ground water varied from 21.2 to 66.6 mg/l, all values were within permissible. The magnesium content varied from 29.22 to 123.40 mg/l hence all the samples were within the permissible limit.

3.4 Total Alkalinity, Carbonate and Bicarbonate

Total alkalinity is a measure of the ability of the water to neutralize acids. The constituents of alkalinity in natural systems include mainly carbonate, bicarbonate and hydroxide. CO_3^{2-} and HCO_3^- may originate from microbial decomposition of organic matter. Alkalinity is a big problem for industries e.g. if alkaline water is used in boilers for steam generation, it may lead to precipitation of sludges, deposition of scales and causes caustic embrittlement. The acceptable limit of total alkalinity in drinking water is 200 mg/l (ISI, 1993). Beyond this limit, taste of water becomes unpleasant, whereas in absence of alternate water source, alkalinity up to 600 mg/L is acceptable. In present study total alkalinity (TA) ranged from 300-790 mg/L. The average total alkalinity was 526.50 ± 13.90 mg/L. The study showed that at all locations

TA was higher than prescribed acceptable limit. Carbonate was absent in all the collected samples, but bicarbonate was present in significant quantities. The bicarbonate content ranged from 300.20 to 955.70 mg/l with a mean of 161.06± 22.59 mg/l which is much higher than WHO limit of 30 mg/l at all the studied locations.

3.5 Sodium and potassium

Sodium and potassium are naturally occurring elements of groundwater. Industrial and domestic wastes also add sodium to groundwater. It is one of the major contributors to salinity of water. The concentration of sodium in the studied samples varied from 52 to 440.80 mg/l. The sodium content has been found to be higher than WHO permissible limit (50 mg/l) at all the studied locations. The potassium content ranged from 1.0-90 mg/l.

3.6 Chloride

Chloride in excess (>250 mg/l) imparts a salty taste to water and people who are not accustomed to high chloride can be subjected to laxative effects (Parkash and Rao, 1989). The chloride content in the studied area ranged from 70.2-295.30 mg/l.

3.7 Phosphate

Phosphate in natural water mostly ranges between 0.005 ppm to 0.020 ppm (Chapman, and Kimstach, 1992).Phosphate may occur in groundwater as a result of domestic sewage, detergents, agricultural effluents with fertilizers and industrial waste water. Its content in present investigation ranges from below detectable levels to 0.40 mg/l.

3.8 Nitrate

Nitrate is the end product of aerobic stabilization of organic nitrogen and occurs generally in trace quantities in surface water supplies but may attain higher levels in some ground waters. Application of fertilizers to land and leaching from cesspools contribute nitrate to ground waters. Nitrate pollution of water is a potential health hazard because consumption of NO_3^- in water can lead to methemoglobinemia particularly in children. The functioning of the central nervous system and cardiovascular system may also be affected by nitrate rich water. The nitrate content in the water samples of the study area varied from 0.0 to 48.50 mg/l. A perusal of data indicates that 17 samples had higher nitrate content than maximum permissible limit of 45 mg/l prescribed by WHO.

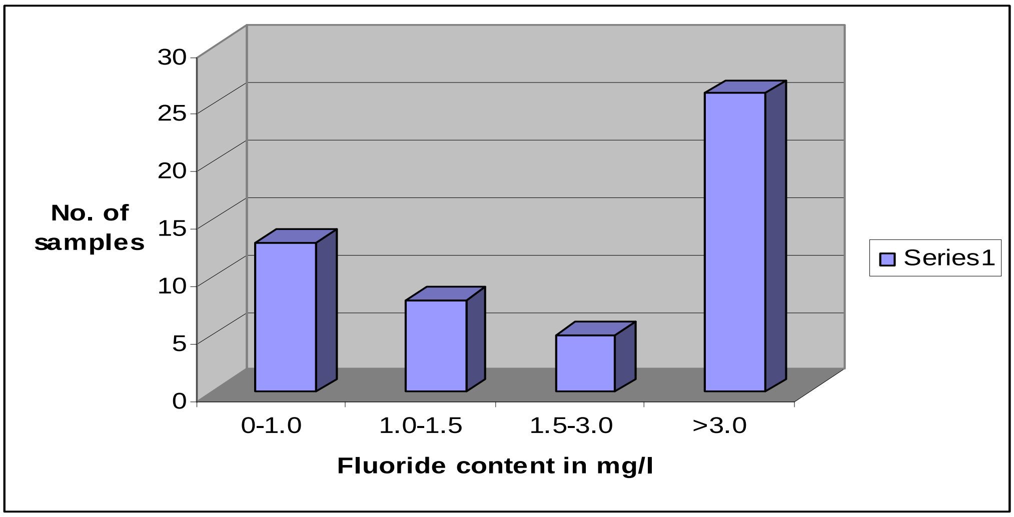

Fig. 1: Frequency Distribution of Fluoride in the Groundwater of Dabwali

3.9 Fluoride

Human body is exposed to fluoride mainly through consumption of water (Singh *et al.*, 2007). The results showed that fluoride concentration in the groundwater of Dabwali ranges from 0.90 – 34.50 mg/l with a mean of 2.20 ± 18.13 mg/l. About 75% (n = 39) have fluoride concentration more than WHO limit of 1.5 mg/l, while 25% (n =13) groundwater samples have fluoride with in permissible limit. The high amount of fluoride present in water may due to leaching and weathering of rocks like fluorspars, rock phosphate and phosphites. The figure-1 shows the frequency distribution of fluoride content in the ground water of Dabwali town of Sirsa, Haryana.

The climate of this region is hot and dry particularly in summer, so higher intake of water is expected by the people. Therefore, the probability of fluorosis is maximum in the study area where mean fluoride concentration in groundwater is 2.20 mg/l. Thus, in this region there is an instant need to warn the people against the threat of dental or skeletal fluorosis and other dysfunctions. People are advised to adopt some techniques of defluoridation of ground water before using for drinking purposes. The high concentration of fluoride in groundwater of study area is may be due to fluoride bearing minerals such as fluorite in the parent rocks of the sediments with in the basin. Apambire *et al*., (1997) have recommended that the main source of ground water fluoride in granitic rocks is the dissolution and anion exchange with micaceous minerals and their clay products. Presence of fluoride bearing minerals in the host rocks and their interaction with water is considered to be the main cause for fluoride in groundwater (Saxsena and Ahmed, 2003) Weathering and leaching of fluorine-bearing minerals in rock formations under alkaline environment lead to the enrichment of fluoride in the groundwater (Raju *et al*., 2009) The important parameters also participate in rock water interaction are concentration of fluoride in rocks, aqueous ionic species and residence time of interaction(Saxsena and Ahmed, 2003)

Fluoride is a highly electronegative element and has a tendency to attract positively charged ions like calcium. Hence the effect of fluoride on mineralized tissues like bones and teeth leading to developmental changes. They have highest amount of calcium and thus attract the maximum amount of fluoride that gets deposited as calcium-flouropatite crystals. Tooth enamel is composed of crystalline hydroxylapatite. Under normal conditions, when fluoride is present in high concentration in groundwater, most of the ingested fluoride ions substitute the hydroxyl ions and formation of fluoroapatite, which is more stable than hydroxylapatite. Thus a large amount of fluoride gets bound in these tissues and only a small amount is excreted through sweat, urine and stool. 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. Excessive intake of fluoride may also lead to muscle fibre degeneration, low haemoglobin levels, deformities in RBCs, skin rashes, depression, gastrointestinal problems, urinary tract malfunctioning, nausea, abdominal pain, tingling sensation in fingers and toes, reduced immunity, repeated abortions, male sterility etc.

4. Conclusions

The present study of groundwater quality with reference to fluoride concentration in the Dabwali, Sirsa district, indicated that the groundwater is slightly alkaline and hard in nature. Fluoride concentration in the groundwater of the study area varied from 0.90-34.50 mg/l. Only 25% water samples are in the permissible limit, prescribed by WHO. High fluoride concentration in the groundwater was found in the study area may be due to the presence of fluoride in the rocks and their interaction with groundwater. Water–rock interaction and evapotranspiration, which were further, influenced by dry climate and low rainfall, these factors of that area played essential role in the alteration of concentration of fluoride in groundwater. It is evident from the results that the people in study area are chronically exposed to higher levels of fluoride and can be indexed as high risk area for dental and skeletal fluorosis.

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