

Distribution of Fluoride in Groundwater and Its Correlation with Physicochemical Parameters

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Abstract: An epidemiological survey was conducted to evaluate the quality of groundwater in 17 villages of Moga district of Punjab, India. Drinking water samples were taken from hand pump, tap and tube wells situated in different localities of the district, for physicochemical analysis. The water quality parameters such as pH, total alkalinity, total hardness, total dissolved solids, calcium, magnesium, chloride, iron electric conductance, and fluoride were measured by using standard methods. The fluoride concentration level in the drinking water of these villages ranged from 0.09 to 10.5 mg/l. The concentration of calcium, magnesium and chloride varied from 8 to 80 mg/l, 9 to 75 mg/l and 22 to 198 mg/l. The values of total hardness and alkalinity ranged from 60 to 290 and 390 to 786 mg/l. Fluoride concentration exhibited significant ($p < 0.05$) positive correlation to pH and total alkalinity and negative correlation to total hardness, calcium and magnesium. Statistical analysis of data revealed significant impact of fluoride on the physicochemical parameters of drinking water samples studied under present investigation.

Key words: Groundwater, fluoride, electric conductance, alkalinity, calcium.

Introduction

Fluoride is one of the chemical elements necessary for human life. Deficiency or excess of fluoride level in the environment is closely associated with human health (Ruikong, 1993). An intake of fluoride in controlled quantities (less than 1 ppm) (WHO, 1997) is known to be beneficial for human health in preventing dental caries, whereas high fluoride concentration in water causes dental and skeletal fluorosis. Drinking water is usually the largest contributor to fluoride intake. Fluorosis is endemic to several countries and is a major menace in India. High groundwater fluoride concentrations associated with igneous and metamorphic rocks such as granite and gneisses have been reported from India, Pakistan, West Africa, Thailand, China, Sri Lanka and South Africa (WHO, 2006). The main reason for the dramatic increase in population exposed to high fluoride levels is the rapid expansion of the deep tube wells for the provision of drinking water in developing countries.

Most of the population in Moga district of Punjab, India use groundwater for drinking purposes. Evidences of dental and skeletal fluorosis in many villages of this district led us to perform an extensive survey of groundwater quality in Moga district with special emphasis on fluoride and to investigate the distribution of natural fluoride levels in water sources and its correlation with other physicochemical parameters.

Materials and Methods

The study area was selected based on general observation of the people suffering from fluorosis. Drinking water samples were collected in clean plastic bottles selected from 17 localities of Moga district, Punjab India. The depth of collected water samples ranged from 45 to 120 m. The water samples were preserved at low temperature and analysed within 48 hours. Fluoride content in the groundwater samples was determined directly after

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dilution with equal volumes of TISAB buffer (pH = 5.2) and the concentration was measured by a fluoride ion selective electrode and a reference pH meter (Orion). The physicochemical characteristics including metals were determined immediately in the lab as per the standard methods for examination of water and waste water (APHA, 2002). Specific electric conductivity and pH are measured by using SEC meter and pH meter. Total dissolved solids were calculated by multiplying the specific electric conductivity with a factor (0.55 to 0.75) that depends on the relative concentration of ions. Total alkalinity was estimated by titrating with H_2SO_4 ; total hardness and calcium were analysed titrimetrically using standard EDTA. Magnesium was calculated on the basis of the difference in the concentration between total hardness and calcium and chloride was estimated by using standard $AgNO_3$ titration. The results obtained were evaluated in accordance with the norms prescribed under Indian Standard Drinking water specification of Bureau of Indian Standard (BIS, 1991).

Results and Discussion

Ground water is the main source of drinking water in rural areas of Punjab, India. The physicochemical characteristics of the ground water samples varied significantly in Moga district of Punjab, India. In the

studied localities ground water was free from colour and odour, and taste was slightly saline in some areas. The pH of all the samples ranged from 7.5 to 8.4 with an average of 7.92 ± 0.58 , which showed slightly alkaline nature of the water. All the samples were found to be alkaline in nature. Trivedi (1988) also found association between fluoride concentration and alkalinity. The total alkalinity of water samples varied from 390 to 786 mg/l with an average of 588.64 ± 113.56 . The value of total hardness ranged from 60 to 282 mg/l (151.52 ± 61.71). Data revealed that the analysed water samples have high alkalinity but have low values of total hardness than the maximum permissible limit (200–600 mg/l). The concentration of fluoride in the groundwater varies from 0.9 to 10.5 mg/l (3.12 ± 2.55) in various localities of Moga district. All the values of physicochemical parameters are given in Table 1.

Calcium and magnesium are important ions for total hardness. Calcium concentration ranged from 8 to 80 mg/l (39.64 ± 28.65). The concentration of magnesium varies from 9 to 65 mg/l (29.56 ± 16.62). A concentration of 30 mg/l is recommended for calcium and magnesium in drinking water, whereas all the studied values were found to be low in water samples. Chloride varied from 22 to 190 mg/l (112.1 ± 47.66). The chloride content was lower than the desirable limit (200–600 mg/l). The

Table 1: Results of physicochemical analysis of selected groundwater samples in Moga District of Punjab, India

Sample Location	pH	TA mg/l	TH mg/l	Ca ²⁺ mg/l	Mg ²⁺ mg/l	F ⁻ mg/l	Cl ⁻ mg/l	SEC	TDS mg/l	Fe ²⁺ mg/l
BoreWala	8.0	776	124	11	23	5.0	72	2270	1340	0.2
Chudchuk	8.1	590	90	10	10.5	5.8	106	2300	1150	0.1
Smadh Bhai	7.9	390	115	24	21	1.9	60	1860	930	0.1
Ganji GulabSingh	8.2	546	60	9	9	5.7	78	1947	890	0.2
Bhloor	8.1	540	100	13	16	2.8	88	1780	620	0.2
Nihal Singhwala	7.9	636	112	27	11	3.7	92	2110	1300	0.1
Badhni Khurd	8.1	424	136	8	28	4.7	22	976	1080	0.05
Roake kalan	8.2	672	80	9	14	2.3	48	3250	760	0.05
Mothanwali	8.4	786	114	22	38	10.5	136	2530	1150	0.15
Moga City	7.7	540	210	45	38	1.1	120	1700	905	0.2
Ajitwal	7.8	490	190	80	65	1.0	138	1970	560	0.1
Kokri Kalan	7.6	610	228	76	41	1.2	116	2110	790	0.1
BadhniKalan	7.5	617	282	71	23	0.9	190	2720	1360	0.05
Bhuttar	7.7	440	210	75	60	0.9	180	4320	2160	0.20
Bilaspur	7.7	610	180	60	45	1.8	135	2750	1375	0.15
Bir Badhni	7.9	710	135	65	32	2.0	160	2900	1450	0.25
BhurjHamira	8.0	630	210	69	28	1.7	165	2480	1736	0.20
Mean	7.92	588.64	151.52	39.64	29.55	3.12	112.1	2351.5	1150.35	0.14
SD	0.242	113.56	61.710	28.653	16.623	2.55	47.664	735.096	410.647	0.0643
Variance	0.1	12896.4	3808.1	821.0	276.3	6.5	2271.9	540365.9	168652.7	0.0

values of specific electric conductivity ranged between 976 to 4320 $\mu\text{mhos/cm}$, which is more than permissible limit (300 $\mu\text{mhos/cm}$). All water samples showed higher electric conductivity that signifies the amount of total dissolved solids in water. Findings of the present study are in agreement with the results of groundwater quality survey conducted by Gupta et al. (1994) in Agra. The total dissolved solids in drinking water reveal the saline behaviour of water, which indicates the organic pollution level of water. The concentration of total dissolved solids ranged from 560 to 2160 mg/l (1150 ± 410.67). It was found to be within limit in all studied samples. Alkalinity showed positive correlation with specific electric conductivity, total dissolved solids and chloride. The results are in consonance with the results of Devi et al. (2003) who analysed the physicochemical characteristics of drinking water of Velsao, Goa, India. It was evident that high concentration of fluoride in water had invariably high alkalinity and low concentration of total hardness, calcium and magnesium. The result of present study revealed a positive correlation between total alkalinity, pH versus fluoride and that negative correlation for calcium versus fluoride. Low concentration of calcium and magnesium in high fluoride water is due to very low solubility of CaF_2 (Gupta et al., 1999; Sarma and Rao, 1997; Kundu et al., 2001).

Correlation matrix for 10 physicochemical parameters of drinking water samples is presented in Table 2. The result showed that most of the parameters bear statistically significant correlation at $p < 0.05$ and indicates close association of these parameters with each other. Results showed a highly significant correlation ($p < 0.05$) between the concentration of fluoride, pH ($r = 0.795$)

and total alkalinity ($r = 0.4207$) in the drinking water (Figures 1 and 2). Scatter plot diagram revealed a strong negative correlation of fluoride vs total hardness (Figure 3). Fluoride concentration is directly proportional with total alkalinity and inversely proportional with total hardness indicating a greater affinity of fluoride with total alkalinity (Rao and Devdass, 2003). Hence, the fluoride content shows an increase with total alkalinity and a decrease with total hardness. A low concentration of total hardness is because of its precipitation as carbonates (Gaciri and Davis, 1993).

Scatterplot diagram indicate a negative significant correlation ($p < 0.05$) between calcium ($r = -0.665$) and the concentration of fluoride in drinking water (Figure 4). Gaumat et al. (1992) recorded negative correlation between fluoride and calcium, in their study on fluoride levels in shallow groundwater of Uttar Pradesh, India. According to Chandra et al. (1981) and Teotia et al. (1981), water with low hardness, i.e. low calcium and magnesium contents, and high alkalinity, presents the highest risk of fluorosis. Similar findings have been reported in a study on fluoride hydrogeochemistry in Ajmer District in Rajasthan, India by Madhavan and Subramanian (2003). They demonstrated the same trend of correlation of fluoride versus total alkalinity and calcium ($r = 0.62$). The mean fluoride concentration in well water varied from 0.1 to 11.6 ppm.

In the present study, a negative correlation of fluoride versus magnesium ($r = -0.310$) has been noted and its correlation was slightly significant at the level of $p < 0.05$ (Figure 5). Our results are also inconsistent with the findings of Smedley et al. (2002), who demonstrated that negative correlation of fluoride with calcium and

Table 2: Showing the correlation matrix among various physicochemical parameters of drinking water samples

Parameters	F	pH	TA	TH	Ca	Mg	Cl	EC	TDS	Fe
F	1									
pH	0.79*	1								
TA	0.42	0.27	1							
TH	-0.58*	-0.74*	-0.26	1						
Ca	-0.67*	-0.78*	-0.12	0.85*	1					
Mg	-0.31	-0.44	-0.13	0.87*	0.71*	1				
Cl	-0.31	-0.52*	0.19	0.52*	0.75*	0.54*	1			
EC	-0.21	-0.19	0.24	0.10	0.27	0.32	0.57*	1		
TDS	-0.07	-0.22	0.12	0.05	0.26	0.22	0.54*	0.64*	1	
Fe	0.22	0.39	0.44	-0.30	-0.09	0.05	0.22	0.45	0.32	1

* Correlations are significant at $p < 0.05$

F - Fluoride, TA - Total alkalinity, TH - Total hardness, Ca - Calcium, Mg - Magnesium, Cl - Chloride, EC - Electric conductivity, TDS - Total dissolved solids, Fe - Iron.

magnesium was due to low solubility of fluorides for these ions. Das et al. (2003), reported the positive correlation of the high fluoride with total alkalinity and negative correlation with the magnesium, calcium and total hardness in groundwater of Guwahati, Assam, India.

Interpretation of hydrochemical analysis revealed that the drinking water in Moga district is hard, fresh to brackish and alkaline in nature. It is concluded that the values of pH, total hardness, total alkalinity, calcium,

magnesium and chloride decreases or increases with increase in the concentration of fluoride in drinking water.

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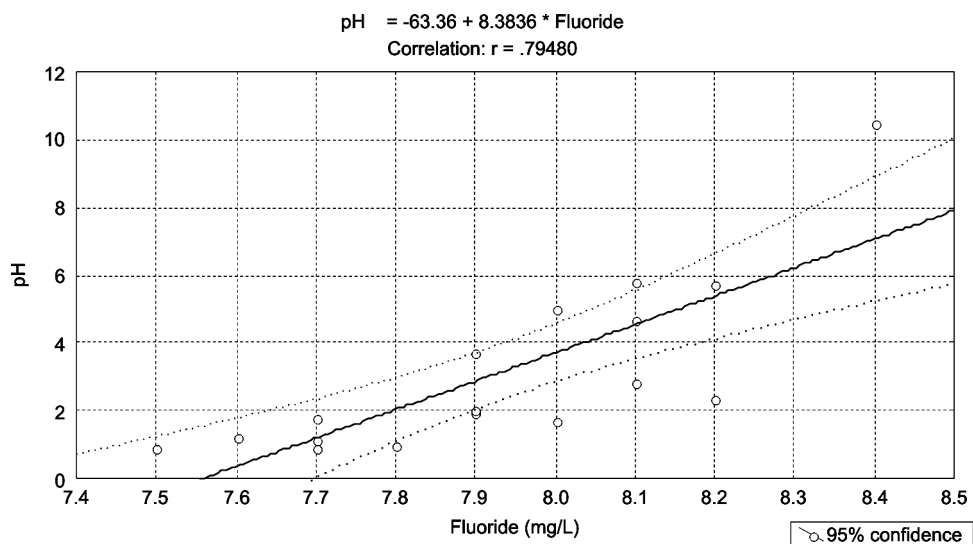


Figure 1: Scatterplot diagram showing the correlation between the concentration of fluoride and pH in drinking water.

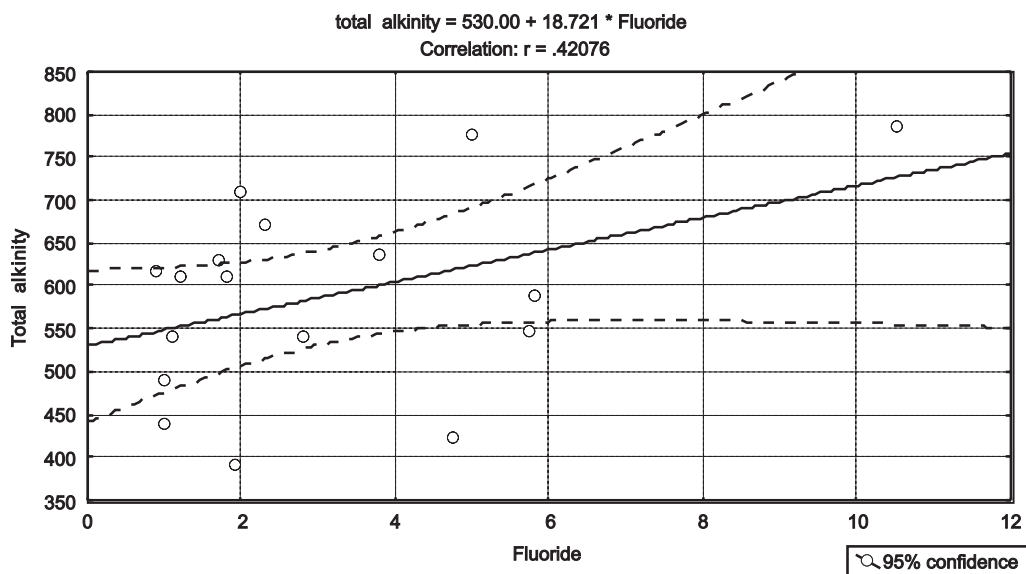


Figure 2: Scatterplot diagram showing the correlation between the concentration of fluoride and total alkalinity.

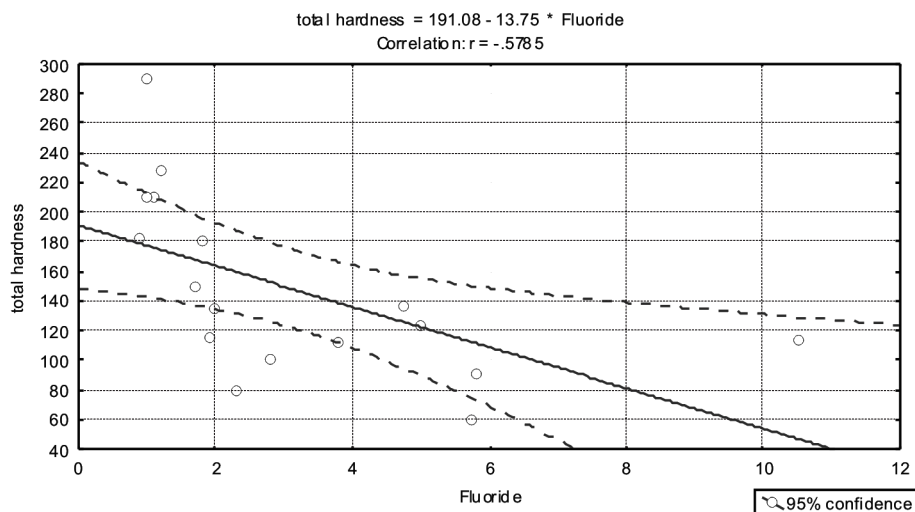


Figure 3: Scatterplot diagram showing the correlation between the concentration of fluoride and total hardness.

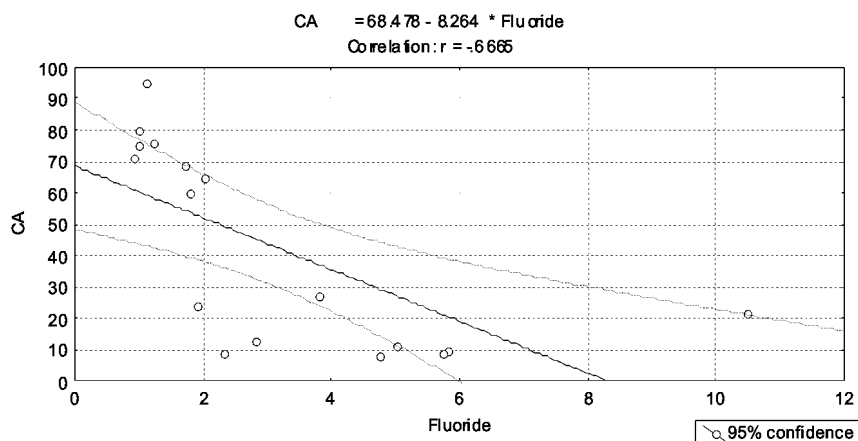


Figure 4: Scatterplot diagram showing the correlation between the concentration of fluoride and calcium.

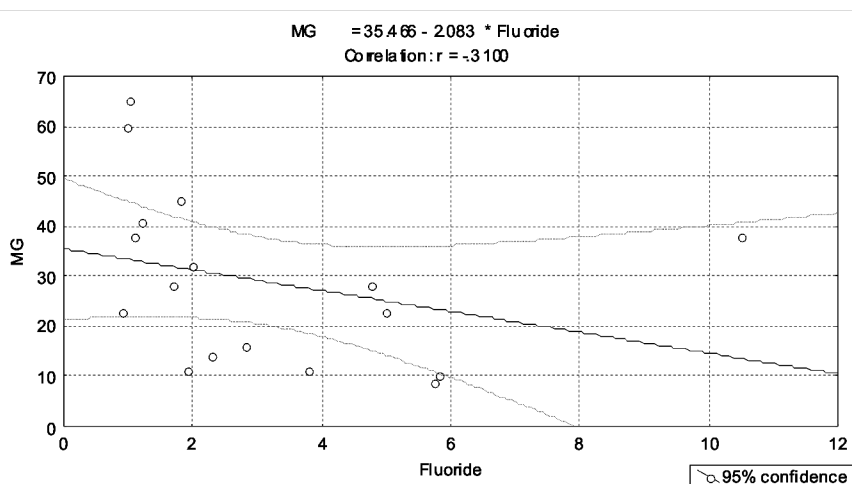


Figure 5: Scatterplot diagram showing the correlation between the concentration of fluoride and magnesium.

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