ISSN Print: 2394-7500
ISSN Online: 2394-5869
Impact Factor: 5.2
IJAR 2016; 2(1): 655-658
www.allresearchjournal.com
Received: 24-11-2015
Accepted: 26-12-2015

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Assessment of water quality with special emphasis on fluoride ions of Udhampur District, J&K, India: Correlation with physico-chemical parameters

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Abstract
Fluoride is a mineral which is naturally being mixed to water in any area and its concentration varies with geographic variations. But present scenario also observes higher concentration of fluoride due to anthropogenic activities. Present work aims to record the fluoride concentration in 25 water bodies, out of which 6 water bodies are lotic and 19 are lentic. The fluoride concentration in water bodies of the study area varied from 0.3 - 1.1 mg/l. Also was recorded a fraction of relation between fluoride concentration and other physico-chemical parameters. It was observed that five parameters viz air temperature, water temperature, pH, bicarbonate and chloride bears a good positive correlation whereas the rest of the three parameters viz calcium, magnesium and total hardness (TH) bears a negative correlation with fluoride.

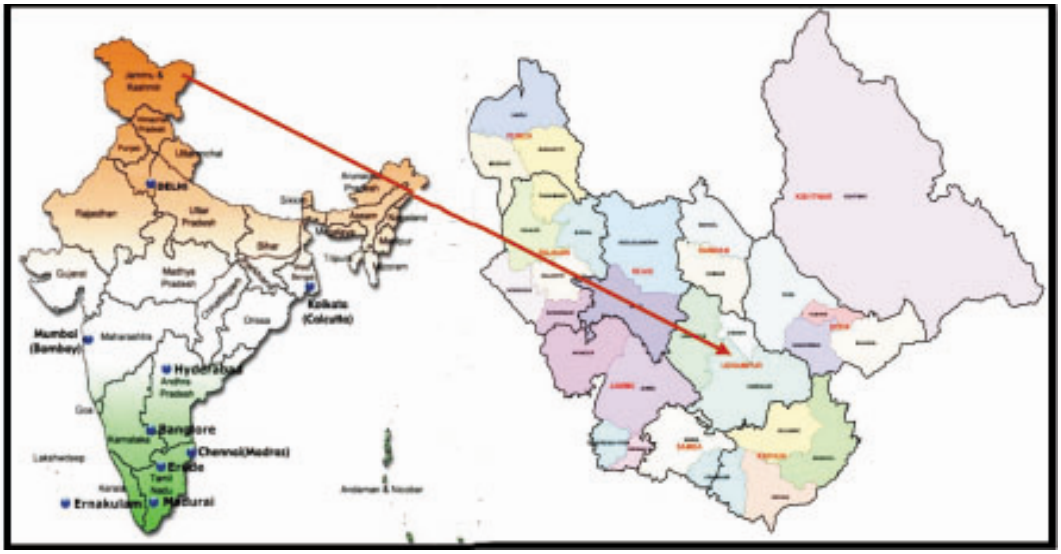
Keywords: Fluoride, water quality, correlation, Udhampur district.

1. Introduction
Environment pollution is the global concern of the day. Water which is essential to life is one of the important component of the environment, which is under threat. Thus, water quality assessment is one of the prime concern and a major challenge. The chemistry of water in any aquatic ecosystem reveals much about the metabolism of that ecosystem and also explains the general hydro-biological relationships existing there (Basavaraja *et al*. 2011) [3]. Quality of water could be rated for various uses like drinking, agricultural, industrial etc depending upon its constituents and minerals and one among them is fluoride.
Fluoride is a naturally occurring compound present in the earth's crust in various forms including-Fluorspar (CaF_2), Cryolite ($NaAlF_6$) and Fluorapatite [$Ca_{10}F_2(PO_4)_6$]. During weathering some fluoride minerals [e.g. Cryolite ($NaAlF_6$)] are rapidly broken down whereas other minerals such as Fluorapatite [$Ca_{10}F_2(PO_4)_6$] and Fluorspar (CaF_2) are dissolved more slowly (WHO, 2002) [32]. In any water body apart from natural process of fluoride addition, anthropogenic sources of fluoride are also there which include the use of chemicals such as CaF_2, NaF, Fluorosilicic acid (H_2SiF_6), Sodium hexafluoride (SF_6) and phosphate fertilizers for various life surviving activities (Pandey and Pandey, 2011). Moreover industrialization has also incorporated a lot of unwanted chemicals along with fluoride in the aquatic ecosystem which hamper the normal functioning of biological pathways in water bodies. The concentration of fluoride above the permissible limits affects not only the formation and working of the calcareous tissue (skeletal and dental) but also has an impact on all soft tissues including liver, brain, kidney, reproductive organs, endocrine glands etc of the inhabiting fauna directly or indirectly through food chain. The effects as per literature are irreversible (SCHER, 2010). With the increasing incidences of fluoride related problems, present study was designed with an aim to chart out a preliminary record for fluoride contamination in drinking water of Udhampur district.

2. Material and methods
Udhampur district is located (32º39'N latitude and 74º35'E longitude) in the south eastern part of J&K state. The district is drained by four major rivers namely Chenab, Tawi, Basantar and Ujh. Groundwater in the area is present under unconfined conditions in the alluvial formations and under confined condition in the underlying rocks of the Shivaliks.

Perennial springs of good discharge are numerous in the whole area and form the principal source of water supply. The sources of the drinking water in the study area are tapwater, bawli, PHE supplies and springs.

The water samples were collected systematically in pre-clean, acid washed (HNO_3 acid) polythene bottles of one litre capacity with necessary precautions from different sites. Water samples were brought to the laboratory for further analysis of various physico-chemical parameters by prescribed standard methods (APHA, 1985).



3. Results and Discussion

Estimation and statistical analysis of various physico-chemical parameters of different locations of Udhampur district, J&K state, India and their comparison with WHO health based drinking water guidelines showed well marked variations (Table 1).

The present survey included various water bodies of Udhampur district which are source of water for basic life activities in different ways. The present data revealed fluoride concentration from 0.3 -1.1mg/l (Table 1) in these water bodies giving a satisfactory note of being within the limits permitted for human use (WHO, 1984). Although within satisfactory limits there appears a great variation in concentration of fluoride from one water body to another which lie in comparable weather conditions. Fluoride concentration in natural water depends on various factors such as temperature, pH, solubility of fluoride bearing minerals, anion exchange capacity of aquifer minerals (OH^- and F^-), the nature of the geological formations drained of water, the contact time of the water with a particular formation and the presence or absence of other precipitating or complexion ions (Largent, 1961; Chandra *et al.*, 1981; Parkhurst *et al.*, 1996; Khaiwal and Garg, 2006) [20, 6, 24, 17].

Table 1: Physico-chemical characteristics of water quality in mg/l except ph and temperature.

S.no.	Sites	Sources	Air Temp.	H_2O Temp.	pH	HCO_3^-	Ca^{2+}	Mg^{2+}	TH	Cl^-	F^-
1	Phangyal	Handpump	27.3	25.3	7.3	190.32	19.34	21.05	106	24	0.62
2	Dhar road	Handpump	27.2	24.1	7.1	180.56	21.03	41.06	190	28	0.61
3	Billan Bauli	PHE Supply	26.1	24.2	7.3	224.48	33.64	42.86	210	42	0.53
4	Kashirah	Stream	26.7	24.1	7.2	165.92	41.2	34.7	184	41	0.34
5	Devika	Bawli	26.8	25.2	7	180.52	26.91	42.06	200	61	0.4
6	Devika	Stream	27.2	24.1	7.4	104.92	39.52	35.59	186	33	0.32
7	Mand East	Tap water	26.2	23.4	7.2	165.92	10.93	46.91	204	42	0.53
8	Malhar	Tap water	25.4	22.4	7.9	224.48	13.46	36.58	164	53	0.64
9	Barnai	Tap water	27.2	24.3	7.4	114.68	11.77	39.42	174	59	0.38
10	Jib	PHE Supply	26.2	24.4	8.1	175.6	21.02	27.94	136	43	0.75
11	Jib	Stream	23.3	18.5	7.3	114.6	11.77	39.42	174	59	0.3
12	Rehmbal	Handpump	27.5	23.4	8.2	183	33.64	37.99	190	42	0.79
13	Gole market	Tap water	23.4	22.4	7.2	148.8	37.84	35.51	184	42	0.31
14	Chopra shop	Tap water	23.8	23.1	8.3	102.48	37	16.76	106	38	0.7
15	Ghari	Well	24.1	16.5	6.8	165.92	26.91	43.03	204	41	0.15
16	Kashirah	Bawli	25.4	25.5	7.6	180.56	39.52	32.67	174	14	0.39
17	Ghari	Nadha	22.2	18.3	7.2	224.48	41.2	34.7	184	27	0.4
18	Phlata	PHE Supply	22.6	25.1	7.3	178.12	18.5	23.69	116	24.2	0.51
19	Tikri	Tap water	23.1	23.2	8.3	224.48	14.29	23.74	112	35	0.6
20	Domain	PHE Supply	24.0	24.2	7.1	165.92	10.09	38.37	168	43	0.66
21	Ramnagar	Spring	23.4	22.0	8.0	258.64	30.2	27.65	144	34	0.72
22	Ramnagar	Spring	24.1	23.4	8.3	300.12	35.3	32.24	168	61	1.1
23		Handpump	23.2	21.2	7.1	185.44	36.16	31.06	164	23	0.40
24	Sudhmahadev	Tapwater	21.0	24.2	7.6	183	19.3	28.35	136	25	0.55
25	Mantalai	Tapwater	20.1	23.5	7.5	212.28	47.0	26.9	158	32	0.46

Table 1 also reveal difference in various other physico-chemical parameters presently recorded. Thus giving an indication of some relation between fluoride concentration and other physico-chemical parameters (Table 2).

3.1 Relationship of Fluoride with pH

In the present findings a positive correlation (r = 0.66) has been observed between fluoride and pH which may be attributed to:

i. pH (and hence alkalinity) influences the fluoride content in groundwater as the alkaline water dissolves fluoride bearing minerals by precipitating calcium and magnesium carbonates simultaneously (Gupta *et al*., 2012) [12].
ii. The ionic radius of the fluoride (0.136 nm) is same as that of the hydroxyl ions which may be easily substituted by one another in water at high pH (Gupta *et al*., 2006 and Sreedevi *et al*., 2006) [10, 29].

3.2 Relationship of Fluoride with calcium and magnesium:

Calcium and magnesium are the essential chemical elements for living organisms and are major material used in mineralization of bone, teeth and shells. These are the most abundant metals by mass in many animals.

The calcium and magnesium ion activity in the natural water is controlled mainly by carbonate ions which form insoluble calcite (Mondal *et al*., 2009) [21]. Thus, the activities of calcium and fluoride and magnesium and fluoride are negatively correlated with a correlation coefficient of r = -0.26 and -0.38 respectively.

Negative correlation of fluoride with calcium and magnesium ions may be attributed to:

i. Low solubility of fluoride from these cation bearing rocks (Sharma *et al*., 2005) [15]
ii. Prior precipitation of calcium and magnesium carbonate from water (Kitano and Okumura, 1973 and Dutta, 2010) [18, 8].
iii. Limited incorporation of fluoride in the $CaCO_3$ structure (Kundu *et al.*, 2001) [19].

3.3 Relationship of Fluoride with Total Hardness

Hardness is an important criterion for determining the usability of water for domestic, drinking and many industrial supplies. During the course of present investigation, Total Hardness recorded negative correlation of r = -0.46 with fluoride because total hardness is the sum of calcium, magnesium, carbonates and bicarbonates. The phenomenon of increased hardness concentration contributing to low fluoride concentration may be attributed to the calcium complexing effect (Ramanaiah *et al.*, 2006) [25]. Present study revealed that Total Hardness reduces fluoride level in water as evidenced by negative correlation between these two parameters. (Trivedi, 1988, Jain *et al*. 2005 and Dutta *et al*. 2010) [30, 15, 8].

3.4 Relationship of Fluoride with bicarbonates:

Perusal of Table 2 revealed that bicarbonate ions show positive correlation (r = +0.29) with fluoride which can be explained by following mass law equation relating calcite and fluorite when both minerals are in contact with water.

$$CaCO_{3\,solid} + H^+ + 2F^- = CaF_2 + HCO_3^-$$

The observed direct correlation between fluoride and bicarbonate ions may attributed due to

i. The release of hydroxyl (OH^-) ions during the leaching and dissolution process of fluoride bearing minerals (Handa, 1975 and Karthikeyan, 2000) [13, 16].
ii. The same ionic radii of F^- and OH^- ions favours the ion exchange process (Vikas *et al*., 2009 and Gnavel and Khan 2013) [31, 9].

3.5 Relationship of Fluoride with chloride ions:

Chloride occurs in all natural water in varying concentrations. In the present study area, chloride ions showed positive correlationship of r = 0.14 with fluoride. This direct relationship is indicative of their similar sources and mobility with fluoride ions (Ramanaiah *et al*., 2006 and Dutta *et al*., 2010) [25, 8].

Table 2: Correlation coefficients among various water quality parameters.

	Air Temp.	H_2O Temp.	pH	HCO_3^-	Ca^{2+}	Mg^{2+}	TH	Cl^-	F^-
Air Temp.	1								
H_2OTemp.	0.52	1							
pH	-0.01	0.21	1						
HCO_3^-	-0.09	0.02	0.05	1					
Ca^{2+}	0.02	-0.03	0.01	-0.03	1				
Mg^{2+}	0.29	-0.26	-0.57	0.03	-0.11	1			
TH	0.29	-0.26	-0.55	0.02	0.22	0.94	1		
Cl^-	0.25	-0.12	0.10	-0.03	-0.29	0.44	0.36	1	
F^-	0.19	0.467	0.66	0.29	-0.26	-0.38	-0.46	0.14	1

4. Conclusion

Thus, it is apparent from the present study that the fluoride concentration of only one station (Ramnagar, 1.1 mg/l) is slightly more than the permissible limit (1.0 mg/l) prescribed by ICMR (1975) [14]. Therefore no dire method of defluoridation are required in the present study area. Some steps towards curbing of fluoride intake can be taken. Detoxification can be done to eliminate the existing fluoride from the body in the form of sweat by regular exercising. A mild modification in dietry habits (e.g. calcium rich diet) and special care in the use of pesticides and fertilizers is recommended.

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