Hydrochemical Studies with Special Reference to Fluoride Hazard in Talwandi Sabo Area, District Bathinda Punjab, India.

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Abstract:*The chemical quality of groundwater in Talwandi Sabo and adjoining areas has been evaluated to understand the factors controlling hydrochemistry and genesis of fluoride. The results of major elements have been used for calculation of cation ratio I ($Na^+ + K^+$)/ (Na^++K^++Ca^+) and anion ratio II (Cl^-/Cl^-+HCO_3^-) which were further plotted against TDS mg/l on Gibbs diagram to know the controls of groundwater chemistry. The findings indicate"Rock Dominance" as the major factor which controls the hydrochemistry of groundwater in the area. Fluoride concentration has been found to range from 0.49 to 2.21mg/l. It shows spatial and temporal variations at micro scale. Fluoride hot spots with concentration more than 1.5 mg/l (WHO limit for drinking water) are common. Fluoride is geogenic in origin and majority samples show negative correlation with calcium and positive correlation with bicarbonate. Sepiolite and palygorskite present in alluvial sediments are the major sources of fluoride. High fluoride in drinking water is responsible for bone and joint problems observed in the population during epidemiological survey. Use of reverse osmosis is recommended to provide safe water supply to alleviate health problems.*

Keywords: *Fluoride, groundwater, geogenic, Talwandi Sabo.*

1.Introduction:

Fluoride in drinking water is an important constituent which is essential when present in small concentration. Deficiency in fluoride has been linked to incidence of dental caries and the use of fluoride tooth pastes and mouthwashes are often suggested by the dentists to mitigate dental health problems [1]. However, excessive concentration of fluoride in drinking water is linked to many dental as well as other kinds of problems i.e. fluorosis etc. Extremely high doses have also been related to cancer [2] though not very well established [3].India is one among the 30 countries, where people consume groundwater with more than 1.5mg/l of fluoride[4], an upper permissible limit prescribed by the W.H.O[5].Nearly 70% of rural world population suffering from fluorosis depends on groundwater.According to WHO [6]guidelines, in areas of warm climate, the optimal fluoride concentration should be below 1mg/l, while in colder climate it could be 1.2mg/l. Since the threshold limitation of fluoride to cause dental/skeletal fluorosis is 1.5mg/l,W.H.O. set the upper limit offluoridein drinking waterat 1.5mg/l. However this guidelineis not universal. For example in India this value is set at 1 mg/l [7].Those affected by fluorosis are from developing / underdeveloped countries whose main source of drinking water is provided by shallow and deep aquifers.

Groundwater with fluoride levels more than 1.5mg/l in general, occur in rocks of granitic composition that contain fluorine bearing minerals such as fluorite, hornblende (F: 5-7%), muscovite (F: 2%) and biotite (F: 5.2%)[8].The solubility of fluorite relative to other fluoride bearing minerals is low [9&10] hence granite with micas and hornblende appear to be the potential source of fluoride in groundwater in granitic terrains[11].

Fluorosis is also commonly reported in arid regions with low rainfall and high evapo-transpiration where weathering rates are high, making the fluorine bearing minerals more susceptible to break down. Low rainfall also promotes long residence time.This enhances the dissolved ions in groundwater. Due to this reason, high fluoride in groundwater and fluorosis are common in semi-arid / arid regions.Nearly 62 million people in arid and semi-arid region of India drink groundwater with fluoride levels > 1.5 mg/l and suffer from dental and skeletal fluorosis [4].

In view of the above, hydrochemical investigations have been carried out in Talwandi Sabo and adjoining areas in Southwest Punjab which are characterised by the arid climatewith a focus on fluoride hazard. In the present paper, results of hydrochemical investigations have been used to find out occurrence of fluoride hotspots in the area. The data of other researchers generated in Talwandi Sabo and in its adjoining areas has also been examined in order to have holistic scenario of thehydrochemical regime and fluoride problem.

2. Location and General Features:

The Talwandi Sabo block forms a part of Indo-Gangetic alluvial plain and lies between 29° 46'30" and 30° 10'5" N latitude and 75° 17'08" and 75° 48'34" E longitude. The block has an area of 77,000 ha and is mostly plain area except around sand dunes which are 2 to 8m above the land relief. The general gradient is from NE to SW direction. The Bhakra Canal (main branch) and the Kotla branch are the major canals flowing through the area. The area lacks proper drainage network and there is only one major drain (Lissara Nallah) in the area. The area has arid and semi-arid climate with an average rainfall of about 300mm. Location of the studied area is shown in Figure 1.

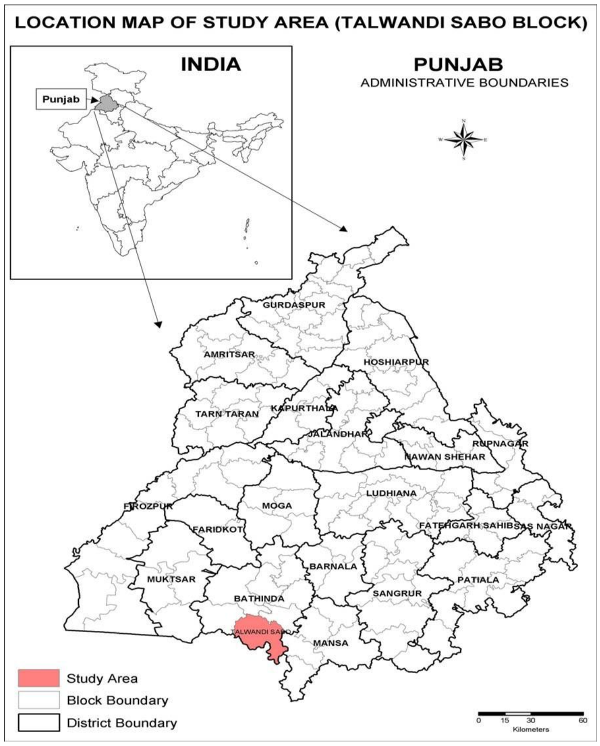

Figure1: Showing location of Talwandi Sabo block.

3. Hydrogeology and Groundwater conditions:

The area comprises of Indo- Gangetic alluvium of Quaternary age. Groundwater mainly occurs in alluvial sediments comprising sands of various grades, silt and gravel beds. Clay lenses are common often having kankar (calcium carbonate concretions). At shallow depth groundwater occurs under the phreatic conditions whereas deeper aquifers occurring at more than 70 m are confined / semi-confined in nature. Regional aquifer system in the south west Punjab is shown in figure 2. The groundwater is saline / alkaline in more than 50 % of the area at the depth of 10 m [12].

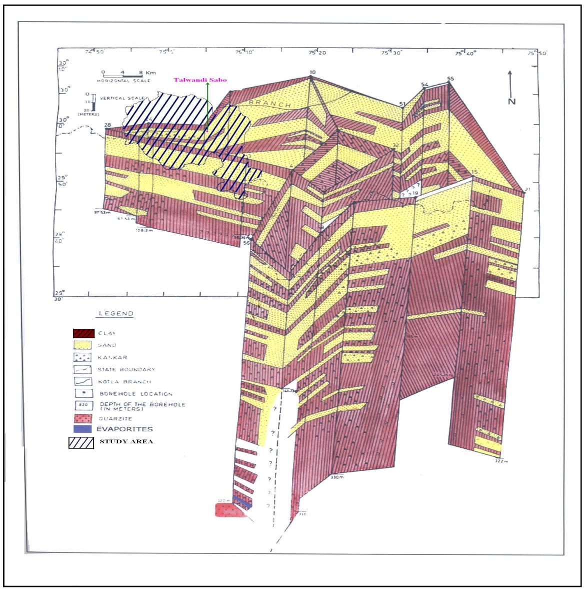

Figure 2: Showing regional aquifer system (modified after Kumar, [13]).

Average depth to groundwater ranges from 5 to 10 m below ground level. Water level elevations above the mean sea level range between 190 to 200 m. Generally ground water flow is from NE to SW direction. Transmissibility of aquifers in district Bathinda ranges from 1300 to 2724 m^2/d and hydraulic conductivity ranges from 1.6 to 19.17 m/d [14]. Water levels in the area have been rising since last more than one hundred years [15]. From the year 1984 to the year 2008, water levels have risen at an average rate of 20-42 cm/year [12]. However, rising water level trend has stabilized now due to exploitation of groundwater by the farmers inspite of poor groundwater quality. This is evident from the increase in the stage of development of groundwater from 48% in the year 2004 to 79% in the year 2008 [12]. The reason for such an increase in stage of development of groundwater is the role of canal seepage resulting in dilution of native groundwater thereby improving its quality otherwise unfit or marginally fit for irrigation use. Farmers get encouraged to install tubewells due to improvement in quality of groundwater.

4. Material and Methods:

In order to evaluate the hydrochemical regime, groundwater samples were collected from the shallow handpumps having depth upto 40 m and tubewells having depth upto 80 m during April 2012 and October 2012. The samples were analysed for major ion analysis and fluoride following standard methodology of American Public Health Association [16]. Fluoride analyses were carried out in the laboratories of PUNSEN, PAU campus, Ludhiana. The results obtained from the chemical analysis of samples collected by authors earlier [15& 17] and have also been used besides using the results of other workers [18, 19, 20, 21] to understand the regional hydrochemical scenario.

5. Results:

The results of the major analysis of samples collected in April 2012 and October 2012 indicate that pH ranges from 8.7 to 9.14; EC ranges from 440 to 6860 µmhos/cm; Calcium ranges from 10.4 to 167.1 mg/l; Magnesium ranges from 10.2 to 167.1 mg/l; Sodium ranges from 15.2 to 315.9 mg/l; Potassium ranges from 10.4 to 310.5 mg/l; Sulphate ranges from 5.7 to 18.4 mg/l; Bicarbonate ranges from 125 to 515 mg/l and Chloride ranges from 4.97 to 440.2 mg/l.These results have been used for calculation of cation ratio I $(Na^+ + K^+)/(Na^++K^++Ca^+)$ and anion ratio II $(Cl^-/Cl^-+HCO_3^-)$ which have been further plotted (Fig. 3a& 3b) on Gibbs diagram [22]. The study of these figures reveals that "Rock Dominance" has acted as a major controlling factor for hydrochemical evolution of groundwater. The minerals present in the sediments have interacted with the water seeping down from canal network, rainfall and return flow of irrigation water. Further, as the area is characterised by the rising water levels since the last century, rising water levels have also interacted with the salts/minerals present in the sediments to enhance the mineralization of groundwater and also increasing groundwater salinity as well as alkalinity.

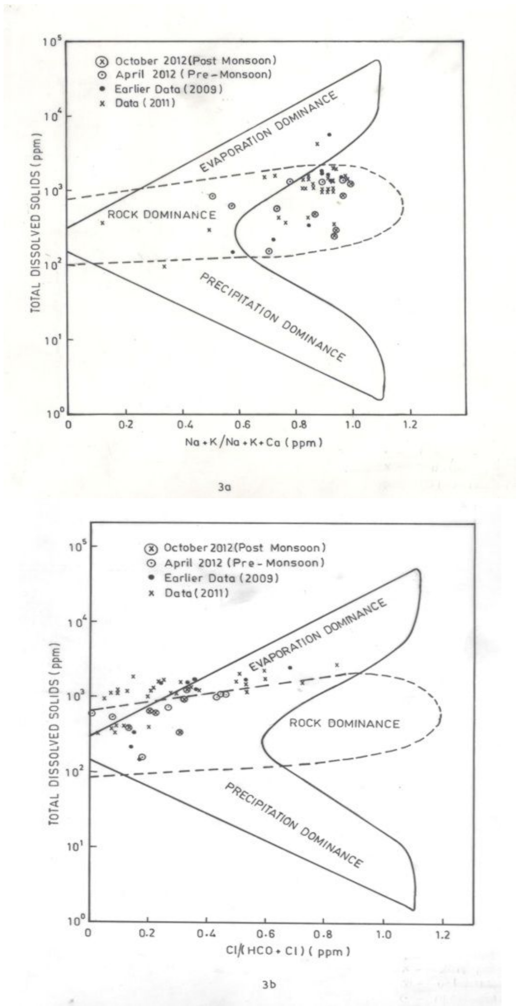

Figure 3a &3b: Gibbs plot for cations and anionsof groundwater samples.

In order to know the hydrogeochemical processes, Chloro-alkaline indices CAI1= Cl- (Na+K)/ Cl and CAI 2 = Cl- (Na+K)/ SO_4+HCO_3+CO_3+NO_3 [23] were calculated to study the process of ion exchange between the groundwater and its host environment (sediments) during water rock interaction. Majority negative CAI 1 and CAI 2 values (Fig. 4&5) noted at Jajjal, Malkana and Gyana villages suggest that magnesium and calcium from water were exchanged with sodium and potassium in rock /sediments favouring cation-anion exchange reactions (chloro-alkaline disequilibrium). However, overlapping CAI 1 and CAI 2 positive and negative values observed in some samples of the area indicate both base exchange and cation - anion exchange reactions took place during water- rock- sediment interaction.

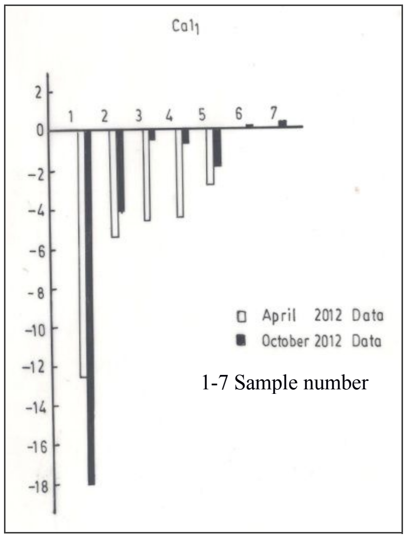

Figure 4: Showing plots of CAI 1values.

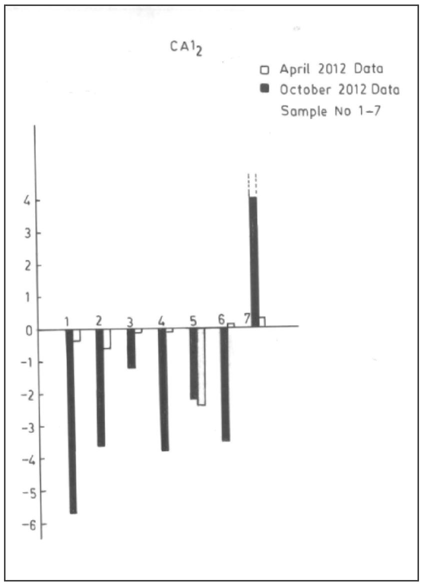

Figure 5: Showing plots of CAI 2 values.

5.1. Fluoride hazard in groundwater:

Fluoride concentration in groundwater drawn from upper unconfined aquifers varies from 0.49 to 2.21mg/l in the area. The regional distribution of fluoride in upper unconfined aquifers is shown in figure 6 based upon data collected earlier [17].Fluoride hotspots having fluoride concentration more than 1.5 mg/l based upon results of samples collected during April, 2012 and October, 2012 and earlier [17]are shown in figure 7.Table I shows villages where high fluoride content(more than 1.5 mg/l) has been found out in groundwater along with the calcium and bicarbonate concentration. Fluoride concentration shows spatial and temporal variations at Jajjal village range from 1.91 to 2.05 mg/l.A limited epidemiological survey was carried out in few villages after doing house to house survey by the Health Department of the State Government. The results of survey are presented in Table II. A perusal of this survey data reveals that large population of the area has bone and joint problems which are attributed to high fluoride water consumption.

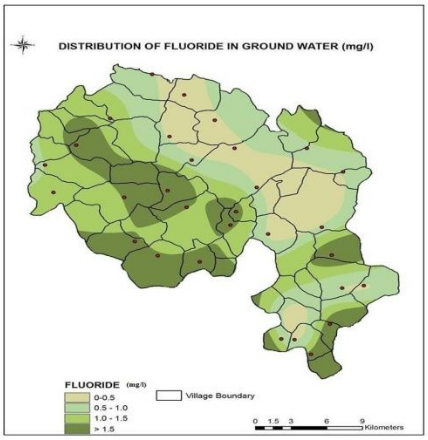

Figure 6: Showing distribution of Fluoride in groundwater of Talwandi Sabo block (after Dhanda [17]).

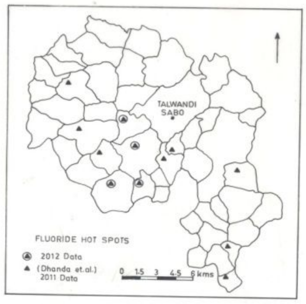

Figure 7: Showing location of fluoride hotspots in the study area.

Table 1. *Showing fluoride content, calcium and bicarbonate concentration hotspots in Talwandi Saboo area.*

Sr. No.	Name of village, owner, type of structure and depth	GPS Location	pH	Fluoride (mg/l)	Calcium (mg/l)	Bicarbonate (mg/l)
1	Burch Maur (Balbir Singh), HP, 30 ft	-	7.10	1.63*	52.1	470
2	Jajjal (Gurudwara), HP, 50 ft	29^0 58’ 07.9’’ 75^0 01’ 48’’	7.26	1.19*	41.6	405
3	Malkana (inside house 1991), HP, 50 ft	-	7.65	1.9*	16.00	320
4	Gyana (Jarnail Singh),TW, 90ft	-	7.85	1.91**	22.6	-
5	Jajjal (Gurudwara), HP, 50 ft	29^0 58’ 07.9’’ 75^0 01’ 48’’	8.83	2.05**	49.6	125
6	Jajjal 2 (s/o Gurinder), HP, 65 ft	29^0 58’ 02’’ 75^0 01’ 42.3’’	8.9	2.21**	15.2	115
7	Malkana (Roop Singh, s/o Banta Singh, HNo. 349), HP, 60 ft	29^0 58’ 03.4’’ 75^0 02’ 16.6’’	8.9	1.85**	16.00	495
8	Gatwali (Sukhdev Singh, s/o Chava Singh), HP, 65 ft	29^0 54’ 06’’ 75^0 02’ 27’’	8.86	1.60**	8.8	650
Earlier Data (Dhanda [17])						
1	Golewala, TW, 46 m	-	7.14	1.85	48.7	310
2	Fatah Balu,TW, 38 m	-	8.15	1.79	41.9	680

3	Talwandi, TW, 18 m	-	8.29	0.42	90.4	515
4	Jajjal, HP, 20 m	-	8.04	2.28	107.2	515
5	Malkana, HP, 15 m	-	8.06	1.53	11.2	730
6	Giana, HP, 15 m	-	8.19	1.58	16	670
7	Gatwali, TW, 39.5 m	-	8.31	1.76	375	310
8	Teona Pujarian, TW, 30.5 m	-	8.17	1.59	117.6	485
9	Sangat Khurd, TW, 24.5 m	-	8.01	1.67	66.4	350
10	Raman Mandi, TW, 26 m	-	8.02	1.56	52.9	350
11	Phulokhari, HP, 23 m	-	8.09	1.57	44	700
12	Bangi Nihal Singh, TW, 27.5 m	-	7.47	1.62	26.8	500
13	Singo, TW, 23 m	-	8.33	1.81	100.9	600

*Pre monsoon, 2012 Data ** Post monsoon, 2012 Data **HP** = Hand Pump **TW** = Tube well

Table II: *Number of patients suffering from various diseases in Jajjal , Malkana, Giana, Shekhpura and Mahinangal villages of Talwandi Sabo block. (Source: Health Department, Punjab)*

Sr. No.	Name of disease	Number of patients
1	Joint pains	463
2	Skin diseases	308
3	Asthma	298
4	Mental retardation	54
5	Congenital defects	47
6	Premature greying hair	38
7	Paralysis	24
8	Numbing of limbs	10
9	Non healing of wounds	4
10	Patients with suspected symptom of cancer	30
11	Cancer deaths in last 10 years	91
12	Cancer cases reported in last 1 year	10

Population surveyed : 13393

No. Of houses surveyed : 3743

5.1.1. Geo chemical relationship of fluoride with major chemical parameters:

An examination of data presented in Table I highlights the following information in groundwater containing high fluoride concentration:

1. High fluoride groundwateris generally associated with low calcium content, there being a negative correlation between the two ions.
2. High fluoride groundwateris generally associated with high bicarbonate ions.
3. At times high fluoride wateris associated with high nitrate concentration as shown in figure8.
4. The groundwater is generally undersaturated with respect to fluorite (Fig.9).

Handa [24] also observed similar relationships in groundwater in the Rajasthan, U.P., Bihar and other states in India.

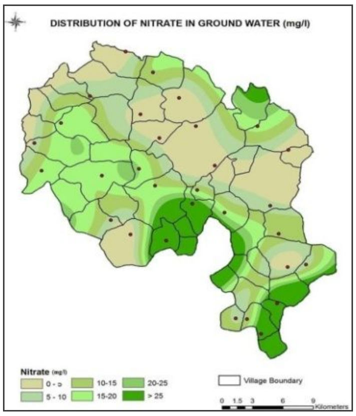

Figure 8: Showing distribution of nitrate in groundwater of Talwandi Sabo block (after Dhanda [17]).

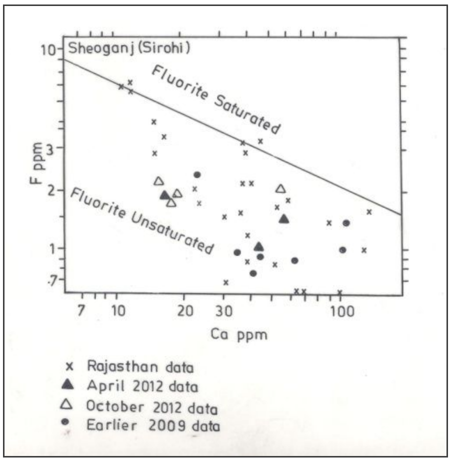

Figure 9: Showing variation of calcium with fluoride in groundwater from the study area (April, 2012; October, 2012 and 2009 data) as well as from alluvium of Sirohi district of Rajasthan (data provided in Handa, 1975 along with saturation curve of fluorite. Groundwater of both the areas shows similar relationship.

5.2. Mechanism of fluoride mobilization or genesis of fluoride rich water:

As already mentioned, the studied area has low rainfall (about 300 mm), arid-semiarid climate and characterized by high evaporation / evapo-transpiration rates. The canal seepages and the rainfall infiltration are the major sources of recharge to the groundwater in the area. These waters are calcium- magnesium-carbonate-bicarbonate types of waters. When water of such chemical composition moves after vertical infiltration along the flow paths, cation-anion reactions take place as has been inferred from the study of CAI 1= Cl- (Na+K)/ Cl and CAI 2 = Cl- (Na+K)/ SO_4+HCO_3+CO_3+NO_3 (Figure 4&5). Sodium from sediments (especially clay minerals) gets released into water resulting into Na-HCO_3 type of water. The alkaline water is effective in releasing fluoride from mineral like sepiolite and palygorskite present in sediments [25]. Therefore, the phenomenon of releasing fluoride from sediments is related to groundwater with residual alkalinity (Ca^{2-} <HCO_3^-) [25]. Evapo-transpiration also leads to precipitation of calcite, a lowering activity and increase in Na/Ca ratio and this allows an increase in fluoride levels from minerals like sepiolite and palygorskite which are the magnesium sinks [26].

9. Conclusions:

The results of major analysis together with Gibbs ratio plots indicate that the chemistry of groundwater in the area is controlled mainly by the chemical interaction between aquifer sediments / minerals and rising groundwater levels as well as infiltrating waters and in addition to evapo-transpiration. Negative CAI 1 and CAI 2 values noted at Jajjal, Malkana and Gyana villages suggest that magnesium and calcium from water were exchanged with sodium and potassium in rock / sediments favouring cation- anion exchange reactions (chloro-alkaline disequilibrium). However, overlapping CAI 1 and CAI 2 positive and negative values observed in the area indicate both ion exchange and cation- anion exchange reactions which took place during water- rock sediments interaction. Fluoride hotspots having fluoride concentration more than

1.5 mg/l i.e. permissible limit of W.H.O.[5] do occur throughout the area and have caused bone and joint problems in the population consuming fluoride rich water. Fluoride concentrations are governed by adsorption equilibrium and fluorite solubility[24]. Evapo-transpiration leads to a precipitation of calcite; a lowering of calcium activity and increase in Na/Ca ratios and this allows an increase in fluoride levels [26]. Fluoride is geogenic in origin. Remedial measures such as providing more canal based water supply and setting up of reverse osmosis plants is recommended where groundwater has to provide domestic water supply.

10. Acknowledgments:

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11. References:

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