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Assessment of Salinity and Fluoride in Groundwater of Semi-Arid Region of Punjab, India

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ABSTRACT

Groundwater is the major source of drinking water in Southwestern semi-arid region of Punjab, India which is now facing severe salinity and fluoride (F^-) problems. A study was carried out in the Bathinda district of southwest semi-arid region of Punjab to assess the salinity and F^- concentrations. Groundwater samples from 21 locations were analyzed, and 59% were found to exceed the permissible electrical conductivity (EC) limit of 1500 μS/cm[1]. Fluoride concentrations exceeded the WHO (2008)[1] permissible limit of 1.50 mg/L in 69% of the samples which may significantly affect human health by causing fluorosis. The increase in groundwater levels leading to high evaporation which caused an accumulation of salts and further resulted in increase in EC. The increased F^- concentration is mainly due to rock-water interactions which led to fluorite dissolution.

Keywords: Groundwater, quality, salinity, fluoride, semi-arid region, South-West Punjab.

INTRODUCTION

The rapid increase in the population accompanied by intense agricultural and urban development has caused a high demand for groundwater resources. This has led to large scale groundwater development, as well as water quality issues and sometimes without responsible management as well as without due attention to quality issues[2]. Fluoride (F^-) is one of the most undesired elements present in underground water extracted for drinking purposes and its presence higher than the prescribed permissible limit may significantly affect human health by causing fluorosis[3,4]. Fluoride is generally present in the naturally occurring minerals fluorite (CaF_2), cryolite (Na_3AlF_6), topaz, tourmaline, muscovite, biotite, hornblende and villianmite[5-9]. Its occurrence in groundwater can be attributed to the weathering and leaching of amphiboles, fluorite, apatite and mica[10-14]. The F^- concentrations are generally found to be higher in water with increasing levels of alkalinity.

In the past 3-4 decades, the Punjab plains have witnessed a rapid rise in groundwater use, which has resulted in its diminished quality and a decline in the water table[15-27]. The deteriorating groundwater quality is mainly due to an increase in groundwater salinity and high F^- concentrations. Causes for the salinity and high F^- concentration are not well understood. This, therefore, has resulted in the current focus on assessing the salinity and F^- concentration in groundwater of the Bathinda district of Punjab, India. The study also examined the concentration and spatial distribution of F^- and its possible origin in relation to geological features of the study area.

MATERIALS AND METHODS

Bathinda district of Punjab was chosen for the present study. The district has total geographical area of 3369 sq. km and has Bathinda, Nathana, Rampura, Phool, Talwandi Sabo, Sangat, Maur blocks. The study area lies between North latitude 29°33' and 30°36' and East longitudes 74°38' and 75°46' in the southern part of Punjab (Fig. 1). It comes under the semi-arid region being near to the desert of Rajasthan with average annual rainfall of 430 mm and is concentrated in the period from July to mid-September. The summer temperature rises as high as 49°C and winter temperature goes down to as low as -1.4°C. The weather is generally dry but is very humid from mid-May to the end of August.

The rocks of the Aravalli-Delhi Supergroup and the Malani Igneous Suite are comprised of greywacke, carbonate sediments, calcareous shale and slate, and the high heat producing granites and felsites form the basement in the region[28-29]. The scattered outcrops of the Aravalli-Delhi Super Group occur at Tusham just south of the study area. Soils in the study area fall in the aridic and moisture regime. Soils associated with the alluvial plains show better indurations with mature development of the soil profile. These are composed of different layers of clay, sticky clay and fine to coarse grained sandstone. The top layer is dark reddish silt and generally rich in concretions and calcareous nodules due to high evaporation. A sequence of halite and associated evaporate (polyhalite, anhydrite, limestone and dolomite) belonging to the Hanseran Group overlie the Jodhpur Group[30]. The dolomite/dolomitic limestone is of a generalized foetid character, related to biogenic reduction and related processes; carbonaceous material and entrapped gas associated with Malout Conglomeratic facies of Tertiary age overlie the evaporate sequence[31]. The geo-morphology, an undulating relief, with around 200 m of poorly preserved, Recent and Sub-recent paleo-surface exists around southwest Punjab, and is also characterized by sandy and carbonate Aeolian material, along with irregular stretches of low-lying sand dunes. Singh (1992)[32] has identified Older plains and Aeolian deposits (both transverse Barchans and longitudinal dunes) in the area.

The groundwater samples were collected from 21 randomly selected sites (Fig. 1) using standard protocol covering all the 7 blocks of the Bathinda district. Wells/tubewells were selected to represent different geological formations as well as land use patterns and different depths (9.14 m – 106.68 m) of the aquifer.

The sub-surface lithology drilled down to 60 m (Fig. 2) reveals an uppermost stratum of clay that is 2-6 m deep. This layer impedes the percolation of surface runoff into the soil, leading to surface flooding and water logging, even in areas having a saturated zone beyond the depth of 6 m. A thick pervious stratum of medium sand is present at a depth of 24-60 m. On a regional scale, this is the only aquifer containing groundwater under phreatic conditions. The depth of water level was recorded using the 'Water Level Sounder' (Eijelkemp,Holland).

All water samples were collected in pre-washed polyethylene bottles. Before taking the sample the hand pumps were properly flushed for at least 5 min and at the time of sampling, bottles were thoroughly rinsed 2-3 times with the groundwater to be sampled. Samples were collected only after electrical conductivity (EC) measurement using an in-situ probe (Mettler Toledo, Sonnenbergstrasse 74 CH 8603 Schwerzenbach, Switzerland) reached constancy and then filtered to separate the suspended sediments. Latitude & longitude of the sample sites were noted using a Garmin global positioning system (Garmin International Inc., Olateh, Kansas, USA). The analysis was carried out as early as possible in the laboratory. The samples were analysed for F^{-} using a calibrated Dionex ion chromatograph ICS-5000 (Sunnyvale, CA, USA) at the Isotope Laboratory, National Institute of Hydrology, Roorkee. The maps of the Figs. 3, 4 and 5 were generated using GIS software, Arc GIS 9.3. There is an interpolation tool in Arc GIS (topo to raster) which used to interpolate a hydrologically correct surface from point, line and polygon data.

RESULTS AND DISCUSSION

Variations of EC and F^{-} concentration in the study area are presented in Figs. 3 and 4, respectively. As evident from Fig. 3, only 41% of the area have EC values below 1500 μS/cm, while 59% have EC values >1500 μS/cm, the prescribed limit for drinking water[1]. The high values of EC are found in the areas adjacent to the Bathinda branch of Sirhind Canal (Fig. 5) and its impact is further extended laterally in the western part due to a rise in groundwater levels. This rise is also due to its reduced use as compared to the canal water, and comparatively warmer temperatures in the summers due to its proximity to the desert[31]. Salinity is caused due to the rise of salts in soils due to the increase in evaporation along the Bathinda branch of Sirhind canal[15] as evident from Fig. 5, where the depth to water level is higher in Bathinda and Sangat blocks.

The values for Ca^{++} varied from 18 to 229 ppm with an average of 78.1 ppm (Table 1). The highest value was found in a groundwater sample from Mehta, and the lowest a sample from Burj Gill. All of the Ca^{++} levels were within the permissible limit of 200 ppm[1] except for the sample collected at Mehta.

Concentrations of F^- ranged from 0.60-4.40 mg/L (Table 1). Water samples collected from approximately 57 % of the study area exceed the permissible limit (Fig. 4) of 1.50 mg/L for drinking water[1].

Fluorine reacts immediately to form F^- compounds due to its high electro-negativity, making

Table 1: Depth, EC, and ion concentrations (Anions-F^-, Cl^-, NO_3^-, SO_4^{--} and Cations-Ca^{++}, Na^+, K^+, Mg^{++}) in South-West Punjab (source: Krishan et al., 2013)[19]

Sampling location	Source	Depth (m)	EC (μScm^{-1})	F^-	Cl^-	NO_3^-	SO_4^{--}	Ca^{++}	Na^+	K^+	Mg^{++}
				Ion concentration (mg/L)							
Mehma Surja	HP	09.14	470	0.0	86.0	3.1	27.10	62.5	22.8	8.8	24.4
Burjmahema	HP	18.29	2890	1.5	210.0	30.1	289.0	41.0	199.0	21.6	39.3
Balluana	HP	30.48	2900	2.6	300.0	217.0	359.0	152.	178.0	75.8	241.0
Phul	HP	30.48	1750	1.1	134.0	17.0	106.0	41.9	124.0	20.2	57.0
Mehta	HP	18.29	3020	4.4	337.0	69.5	529.0	229.0	168.0	30.0	218.0
Phul-300	TW	91.44	1800	0.6	152.0	55.1	164.0	120.0	127.0	20.1	98.4
Bhairupa	TW	106.68	1260	0.9	87.5	11.2	161.0	52.0	88.5	15.9	45.2
Bathinda	HP	30.48	2995	1.1	205.0	166.0	228.0	116.0	154.0	42.0	79.6
Rama	HP	21.34	1170	2.2	22.4	62.0	51.40	116.0	10.2	105.0	135.0
Rampura	HP	30.48	1360	1.8	149.0	0.0	123.0	70.9	123.0	27.5	77.2
Jhumba	HP	24.38	1890	3.6	37.3	16.9	153.0	25.3	142.0	16.4	21.3
Khemuana	HP	30.48	1200	1.8	51.0	12.0	146.0	77.4	85.3	19.4	90.4
Ablu	HP	18.29	3000	0.8	167.0	113.0	229.0	52.0	127.0	105.0	89.3
Bagha	HP	18.29	1940	0.6	176.0	32.0	321.0	107.0	129.0	34.2	97.1
Jalal	HP	45.72	800	2.0	7.3	7.2	47.80	41.5	20.0	199.0	37.1
Bhikianwalai	HP	19.81	1760	0.7	62.3	46.6	69.40	37.0	23.6	8.2	43.9
Burj gill	HP	48.77	1600	3.3	33.6	10.8	70.60	18.0	129.0	9.8	0.0
Ramgarh	HP	18.29	3000	2.1	502.0	79.9	784.0	58.6	509.0	61.3	62.5
Maur	HP	30.48	1400	3.8	29.6	21.2	124.0	33.6	146.0	17.6	0.0
Sheikhpura	HP	30.48	1160	1.7	59.2	2.7	119.0	101.0	74.8	23.9	77.3
Bhagibanda	HP	30.48	800	0.8	22.9	5.4	45.1	87.4	4.70	9.9	33.8

HP= Hand pump; TW= Tube well

the presence of free fluorine a remote possibility. Under favourable physico-chemical conditions with long residence time the fluorine may occur in dissolved form in groundwater[5,33].

The groundwater analysis showed that sodium (Na^+) values range from 4.7 mg/L to 509 mg/L and the potassium (K^+) values range from 8.2 mg/L to 199.0 mg/L. The chloride (Cl^-) values range from 7.3 mg/L to 502 mg/L and the nitrate (NO_3^-) values range from 2.7 mg/L to 217 mg/L. The sulphate (SO_4^{--}) values ranged from 27.1 mg/L to 784.0 mg/L.

The water level depth in Bathinda district ranged from 6.9 to 15.4 m (Fig. 5). Existence of fresh water zones upto deeper levels, as have been established in the current work in the Phul and Nathana blocks, reflect on the declining water table levels and the consequential difficulty of its extraction[22].

During weathering and circulation of water in rocks and soils, F^- can be leached out and get dissolved in groundwater. The variation in F^- concentrations of groundwater depends on the geological settings and type of rocks. The F^- concentration of groundwater is also influenced by the presence of other ions. A moderate positive relationship between F^- and Ca^{++} (Dancey and Reidy's, 2004)[34] was observed (r=0.77, R^2=0.59; p-value=0.0013 at p=<.01; df =14) in the samples collected from the depth=18-45m and where NO_3^- concentration is <80mg/L. Strong positive

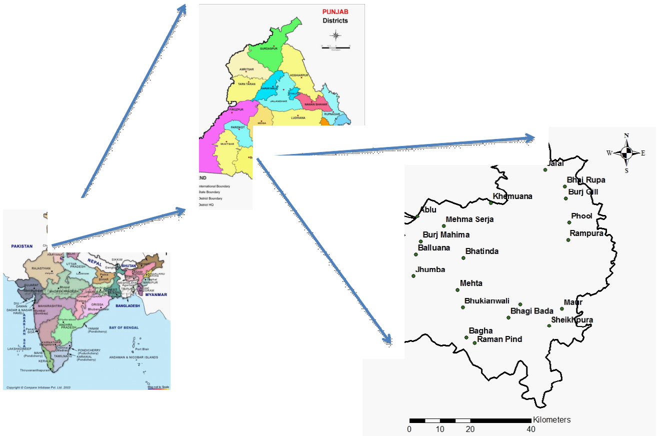

Fig. 1: Study area with sampling points

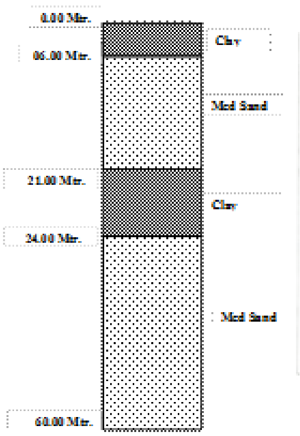

Fig. 2: Litholog of the Bathinda district

significant correlations were also observed between Na^+ and Cl^- (r= 0.84, R^2=0.71, p-value=0.00001 at p=<.01; df =19); Na^+ and SO_4^{++} (r= 0.89, R^2=0.78, p-value=0.00001 at p=<.01; df =19); Cl^- and SO_4^{--} (r= 0.94, R^2=0.89, p-value=0.00001 at p=<.01; df =19). A moderate positive non-significant correlation was observed between Mg^{++} and SO_4^{--} (r= 0.45, R^2=0.20, p-value=0.0532 at p=<.01; df =19).

High F^- concentrations are linked to high sodium contents, high pH and low Ca^{++} concentrations[35]. The weathering of Na^+ rich sediments increases pH which in turn triggers the dissolution of CO_2. The consequent increase in HCO_3^- and CO_3^{--} causes oversaturation in the groundwater compared to calcite, leading to precipitation of this

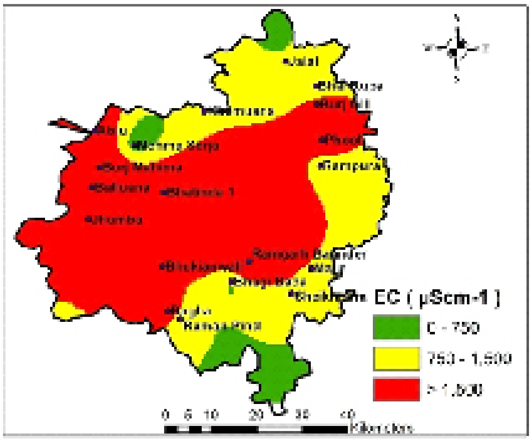

Fig. 3: EC map of the study area

mineral. This precipitation lowers Ca^{++} concentrations in solution and leads to a sub-saturation for fluorite in the system. As a result, fluorite will dissolve and F^- concentration will increase (equations 1-5). The samples from Burj Mehma, Phul, Rampura, Jhumba, Khemuana, Burj Gill, Jalal, Ramgarh, Maur with low Ca^{++} concentrations are typical of high F^- groundwater.

$$CaCO_3 \longleftrightarrow Ca^{++} + CO_3^{--} \quad K=10^{-8.4} \quad ...(1)$$

$$CaF_2 \longleftrightarrow Ca^{++} + 2F^- \quad K=10^{-10.57} \quad ...(2)$$

$$CaF_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2F^- + 2Na^+ \quad ...(3)$$

$$CaF_2 + 2NaHCO_3 \longrightarrow CaCO_3 + 2F^- + 2Na^+ + H_2O + CO_2 \quad ...(4)$$

$$2Na(AlSi_3)O_8 + 2H^+ + 9H_2O \longrightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 4H_4SiO_4 \quad ...(5)$$

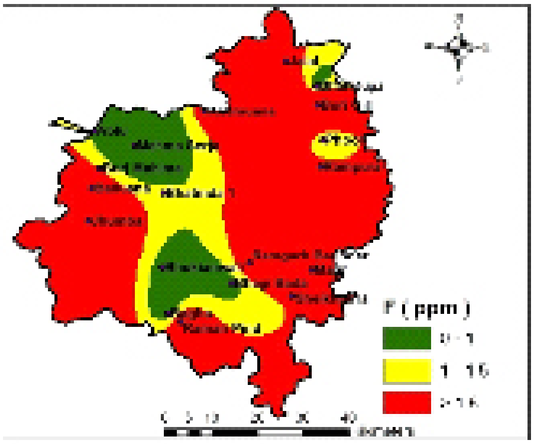

Fig. 4: Fluoride map of the study area

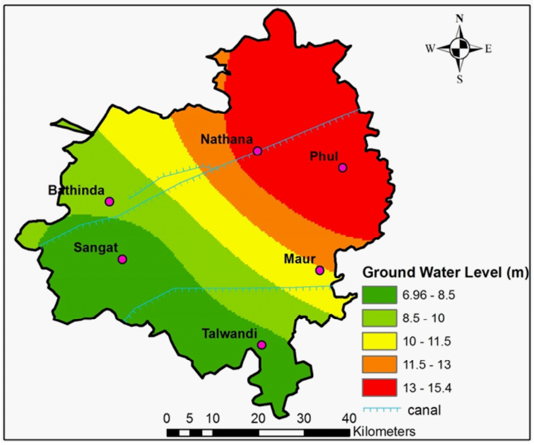

Fig. 5: Depth to water level map of Bathinda district

A weak negative statistically non-significant relationship[34] between F^- concentration and sampling depth ($r=-0.14$; p-value=0.545 at $p=<.01$; df =19) was observed. The concentration of F^- in groundwater largely depends on reaction times with aquifer minerals. Groundwater with long residence times in aquifers has high F^- concentrations and these are associated with deep aquifer system and a slow groundwater movement. Accordingly, shallow aquifers which contain recently infiltrated rainwater usually have low F^- concentrations. In arid/dry conditions groundwater flow is low and the reaction time of groundwater with the rock is long[36] which creates more time for dissolution of fluoride bearing formations. But the higher concentration in the samples taken from shallow depths may be due to increased water levels as a result of evaporation[19].

A weak positive non-significant relationship[34] between F^- and EC was obtained ($r=0.23$; p-value =0.3202 at $p=<.01$; df =19). In a range of specific conductivity between 750 and 1750 ìS/cm, dissolution rate of fluorite minerals increases[37].

Thus high concentration of fluoride is due to (i) its geo-genic origin (ii) high evaporation. Due to evaporation, the groundwater gets oversaturated with calcic minerals, resulting in precipitating of calcite, resulting in dissolution of fluorite[38].

The study of groundwater quality with emphasis on F^- concentration in southwest Punjab indicated that the high concentration of F^- was substantiated by EC and various geochemical processes such as ion-exchange, dissolution and weathering. The groundwater in the area is saline and highly contaminated by F^- and it was found more than 2/3rd part of the study area has higher concentration of fluoride (above permissible limit of WHO (2008)[1] and BIS)[3]). Thus low rainfall coupled with high evaporation rate, highly variable diurnal temperatures, alkaline environment and long residence time favors dissolution of F^- in groundwater.

The areas with increased water level in the southwest, Punjab are likely to get water logged in near future which can be seen in Fig. 5 and also reported by CGWB (2007)[15] and Krishan and Chopra (2015)[23]. Due to this reason, there is an urgent need to arrest the rising water trend in southwestern part of the district and implement anti-water logging schemes. For controlling the deteriorating quality with respect to F^- concentration in semi-arid region of Punjab, suitable management practices can be undertaken. Conjunctive use of surface and ground water needs to be done to overcome the water level and groundwater quality problems. For this, in the southern part of the district where excess surface water is used, the usage of groundwater is to be encouraged. The causes for F^- contamination are mostly natural and inevitable, therefore, educating the people and de-fluorinating the groundwater before consumption are essential for maintaining a supply of healthy potable water.

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