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Delineation of safe groundwater aquifers in a Fluoride contaminated region: Walwa Taluka, Maharashtra

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Abstract. Groundwater aquifer contamination has leads health problems in village areas of Maharashtra, India. In this study, groundwater analysis was carried out for different groundwater parameters along with fluoride to delineate the high and low contaminated fluoride region in the Walwa taluka, Maharashtra. A distinct contaminated regions for high and low F^- contaminated regions were identified in the collected post monsoon groundwater samples (n = 144). In total 98% samples are unsuitable for consumption. Hydro-geochemistry of the region showed highest anion concentration for bicarbonate (1880 mg/L), whereas highest cation concentration for calcium was measured as 118 mg/L. It is main cause for alkaline groundwater condition in this region. The 2D ordinary kriging results are well corborated with the obtained hydrogeochemistry results. The low F^- concentration region was found near the Krishna River, whereas high concentration regions were found near the agricultural and high land region. The primary hydrogeochemistry of the region suggests that the geogenic source of F^- minerals in the region. The practice of fertiliser, herbicides and pesticides on agricultural field suggests that these are the secondary source for groundwater F^- contamination. The applied numerical groundwater modelling software, provided technically viable and effective decision making-tool for identification of safe region in the study area.

1 Introduction

Potable water sources are the predominant natural source for supporting life on earth, such as surface water bodies and groundwater (GW) at different depth aquifers [1]. Severe deficiency of potable and palatable water for drinking and other usages is a major problem facing many developing and developed countries [2]. To meet the increasing demand of developing and developed countries for usage of drinking, domestic, agricultural, and industrial purposes, peoples are mostly relying on GW sources in that region. However, due to rapid growth of industrialisation and agricultural activities GW quality of the South Asian

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countries are deteriorating and causing health problem to humans at local regions [3]. Researchers have reported that in total 79 % of the diseases are prevailed due to drinking of contaminated groundwater and out of which 60% diseases are reported caused by drinking high fluoride (F^-) containing water.

Optimum F^- concentration of in drinking water help to protect dental development and bone strengthening, whereas concentration less than 0.5 mg L^{-1} and more than 1.5 mg L^{-1} leads to chronical diseases [4, 5]. The reported chronical diseases due to less (i.e., 0.5 mg L^{-1} and high (i.e., 1.5 mg L^{-1}) consumption of F^- are skeletal fluorosis, renal, neuronal disorders and at sever condition myopathy patient also reported [6]. Human body daily requirement of F^- is 0.05 to 0.07 mg. per kg of body weight [7,8]. Researchers have found primary sources of fluoride in groundwater is F^- bearing secondary minerals viz., muscovite, biotite, granites, quartz, and alkaline volcanics [7]. Often F^- containing minerals are found in metamorphic and igneous rocks [8, 9].

Asian countries severely affected by high F^- groundwater contaminations especially India, Bangladesh, and China, whereas in India, 29 states, have reported high F^- contamination in groundwater [8,9]. Lower F^- concentration has reported in near Varnasi, Uttar Pradesh state whereas the highest concentration reported in Punjab state. In Maharashtra, 7 district have reported high F^- contaminated district namely Akola, Amravati, Bhandara, Buldhana, Chandrapur, Jalgaon, Nagpur, Nanded, Solapur and Yavatmal [10].

In western Maharashtra, till no such severe cases has reported. Aim of this study is to identify in high and low F^- concentrated regions in Walwa Taluka, Sangli District of Western Maharashtra. Also, prepare spatial distribution map for the region to delineate the high and low F^- contaminated area in the study area. Therefore, understand F^- occurrence and its spatial distribution at different depth of aquifers is a major concern facing many organisations to managing GW water resources.

1.1 Study area

In western Maharashtra, Walwa taluka located between latitude 17.0256° N and longitude 74.3762° E in Sangli district. The Walwa Taluka geographically falls under the semi-arid of Maharashtra state, India, which receives annually 580 mm (viz. average) precipitation. The geology of the area mainly comprised by Cretaceous-Eocene age, which is usually known as deccan traps. It consists of thick layer of basalt and igneous rocks, metamorphic at an around 100 ft below the sedimentary rock layer from the ground surface.

1.2 Groundwater sampling

The groundwater samples were collected from deeper and shallow depth bore wells and essential information were recorded on site. In total 144 GW samples were collected in 250 mL capacity bottles (Tarson, India) [11]. The GPS coordinates was recorded during the sampling using Garmin Montana 610 for each location. The samples were filled in bottles by ensuring that there is no leakages and do not exposed to the natural environment.

2 Materials and Methods

2.1 Groundwater analysis

The essential groundwater parameters were analysed on field using multi-parameter water testing kit such as oxidation-reduction potential (ORP), dissolved oxygen (DO), electric conductivity (EC), total dissolved solids (TDS) and temperature. The field results were recorded after pH and DO concentration gets stabilized. The standard water testing method recommended by American Public Health Association (APHA 2017) was followed for cation and anion concentration détermination [5]. The dissolved concentration of Ca^{2+}, Na^{+}, K^{+} cation was measured using a flame-photometer (Systronics flame photometer 128, minimum detention time limit is 1.0 mg L^{-1}) instrument [12,13]. The anions concentration were measured by different methods such as for bicarbonates (HCO_3^-) and Cl^- were calculated by titration method, and fluoride (F^-) was measured with the help of SPANDS (viz. Method 8029) reagent solution using portable F^-testing kit (Hanna, HI 93729, ISM) [14,15].

2.2 Ordinary Kriging

Spatial data interpolation was carried out to determined using 2D Kriging method [3,11]. At the unsampled site, using this kriging method with a combination of different variograms, determined the concentration over the study area. Following ordinary kriging method equations was solved;

$$\gamma(\bar{x},\bar{y}) = \frac{1}{2N} \times \sum(Z(\bar{x}) - Z(\bar{y}))^2 \qquad (1)$$

Where, variables at the point $\bar{x}$ and $\bar{y}$ are Z($\bar{x}$) and Z($\bar{y}$) and 'N' is a number of data pairs. Variogram in the form of $'\gamma$(h)' it is based on the planar distance of 'h' between two points $\bar{x}$ and $\bar{y}$. The following equation was used in the ordinary kriging method :

$$Z(\bar{\bar{x}}) = \sum_{i=1}^{N} \lambda_i \times Z(\bar{x})i \qquad (2)$$

Where the estimated and observed values at a point $\bar{\bar{x}}$ is Z ($\bar{\bar{x}}$) and at 'i^th^' point $(\bar{x})i$ is $Z(\bar{x})i$. The observed value in the λ_i point is the weight of $(\bar{x})i$. Semi-variogram models gaussian model was used for in 2D kriging method.

$$\gamma(h) = C_0 + C\,(1 - \exp\left[-\left(\frac{3h}{a}\right)^2\right] \qquad (3)$$

Where 'C'is the sill ; 'C_O' is the nugget effect; 'h' distance in meter and 'a' is the range of values.

3 Results and Discussion

3.1 Groundwater Hydrogeochemistry

The analysis data summarised in Table 1 as minimum (Min.), maximum (Max.), average (Avg.) obtained for post monsoon season samples. The pH ranges between 5.1 to 8.4 in post monsson season. In alkaline groundwater is hydroxyl (i.e., OH^-) ions quickly replace [8,11]. The average concentration measured for EC, TDS, DO as 1615.1 µs/cm, 848.6 mg L^{-1}, 3.3 mg L^{-1} respectively. The concentration of anions Cl^-, $F^-$and $HCO_3^-$was varied between 10.5 mg L^{-1}, 826.5 mg L^{-1} and 0.4 mg L^{-1} respectively. In statistical method, fluoride shows a significantly positive affinity with pH, $HCO_3^-$and Na^+ which suggest the primary cause for alkalinity of GW and can promote the further solubility of fluorite mineral in the aquifers [8]. High HCO_3^-, Na^+ and alkaline pH also found responsible for release of fluoride and ion exchanges phenomenon by hydroxyaminos in aquifer [8]. Moreover, in the bicarbonate and sodium facies also enhance the solubility rate of F^-in GW aquifer [9]. The F^-concentration determined was in the ranges of bdl to 1.29 mg L^{-1}, with mean 0.4. The 2D ordinary kriging method, shows distribution of dissolved concentration of F^-over the study area (Fig.1), which occurred due to presence of F^-bearing minerals in the study area aquifers [11]. It is

Table 1. Hydrogeochemistry of the post monsoon GW samples (n=142)

Parameters	Post monsoon season (in 2022)		
	Min.	Max.	Avg.
pH	5.1	8.4	7.4
ORP (mV)	25.2	131.2	76.4
DO (mg L^{-1})	0.9	4.5	3.32
EC (µS/cm)	290	9868	1615.1
TDS (mg L^{-1})	6.6	5603.6	848.6
Temp. (°C)	27.5	57.6	27.9
F^- (mg L^{-1})	bdl	1.3	0.4
HCO_3^-(mg L^{-1})	448	1880	826.6
Cl^-(mg L^{-1})	5.5	26.9	10.5
Na^+(mg L^{-1})	bdl	106.4	5.6
K^+ (mg L^{-1})	bdl	140.1	9.7
Ca^{2+} (mg L^{-1})	bdl	477.6	80.5

Note: below detection limit is abbreviated as 'bdl'

assisted to show the GW movement and demarcate the low concentration aquifer region in the study area. The region near Borgaon and Walwa villages, the infiltration from Krishna River water found, which inevitably dilutes the dissolved concentration of F^-in the different depth aquifer. Comparatively high F^-concentration regions was measured in Industrial and agricultural area of Islampur MIDC area and in Kasegaon & Walwa villages.

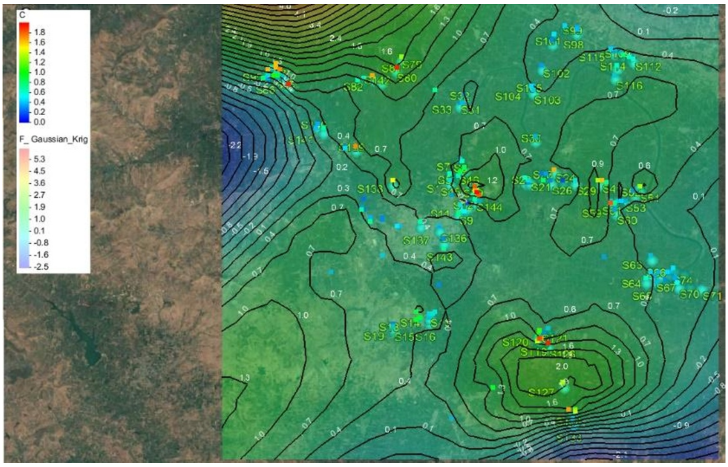

Fig. 1. 2D Spatial Distribution map for F^-concentration in aquifer GW

4 Conclusion

This primarily study on groundwater chemistry implies that the Ion exchange and mineral dissolution are the major phenomenon causes low and high F^-concentration in study area. The comparatively minimum dissolved F^- concentration in the region suggest that the fluoride get saturated in fluorite mineral and can be dissolve in slightly alkaline groundwater condition. The measured F^-concentration was between bdl to 1.3 mg L^{-1} with uneven pattern in the different depth aquifers. In the hydrogeochemistry results 45 % low (i.e., <0.5 mg L^{-1}, n = 64) and 4% high (i.e., >1.5 mg L^{-1}, n = 4) are unsafe according to WHO standard drinking limit. The safe region was identified near the riverine area, whereas, heterogeneous distribution found near the hilly area were season agricultural practices are carried out. This study indicates that shallow depth aquifers are highly vulnerable to aquifer flushing and infiltration from surface water bodies. Therefore, the measured fluoride concentration in collected GW samples is not within the permissible limit hence, the groundwater is inadvisable for drinking and irrigation usage. The high dissolved F^{-} concentration in the region is predominantly dominated by F^{-}bearing minerals dissolution and weather in alkaline groundwater aquifer. The key findings of hydrogeochemistry, provide valuable input for managing the demand for drinking irrigation, and industrial purposes.

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