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Assessment of Drinking Water Quality with Special Reference to Fluoride: A Case Study of Varanasi District, Utter Pradesh, India

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ABSTRACT In the present study, detail investigation of groundwater for the suitability of drinking purposes in Varanasi area. For this purpose, 42 groundwater samples from shallow hand pump and deep hand pump wells and tube wells were collected and analyzed. The pH values reveal that the groundwater is alkali in nature. The quality assessment shows that in general, the water is suitable for domestic purposes. Total dissolved solids of all of analyzed groundwater samples were falling in the category of fresh water. HCO_3^- and Cl^- are dominant anions and Na^+ and Mg^{2+} as the dominant cations in the water chemistry. The sequence of the abundance of the major ions is in the following order: $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+ = \text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{F}^-$. The concentrations of major ions in groundwater are within the permissible limits for drinking except fluoride. The amount of total dissolved solids was less than 300 mg/L, indicating a “fresh environment”. In majority of the samples, the analyzed parameters are well within the desirable limits and water is potable for drinking purposes. However, concentrations of Total hardness, Na^+ , Mg^{2+} , K^+ and fluoride exceed the desirable limit at few sites.

KEYWORDS: Groundwater quality Fluoride Fluoride Geochemistry Varanasi.

I. INTRODUCTION

Groundwater forms the major source of water supply for drinking purposes in most parts of India. It accounts for about 88% safe drinking water in rural areas, where the population is widely dispersed and the infrastructure needed for treatment and transportation of surface water does not exist. The quality of groundwater depends on various chemical constituents and their concentration, which are mostly derived from the geological data of the particular region. Water quality is the characteristics of water which influence its beneficial use as well as the sustainability of ecosystem. Water resources are of critical importance to both natural ecosystem and human development [1]. Ground water quality is being increasingly threatened by rapid increase in population and growth of industrialization, use agricultural chemicals and disposal of urban and industrial wastes. It has been estimated that once pollution enters the subsurface environment, it may remain concealed for many years, becoming dispersed over wide areas of groundwater aquifer and rendering ground water supplies unsuitable for consumption and other uses. The deterioration of ground water quality is of immediate concern in the districts, cities and towns of the country. [2] [3] [4] [5] [6] [7] [8] [9] [10] [11][12] Today, water quality issues have become a significant concern due to the growth of population, urban expansion and technological development. Water can be easily contaminated in different ways through unregulated or regulated but not well designed and monitored disposal [13] Public ignorance of environment and related considerations, lack of provisional basic social services, indiscriminate disposal of increasing anthropogenic wastes, unplanned application of agrochemicals, and discharges of improperly treated sewage/industrial effluents; result in excess accumulation of pollutants on the land surface and contamination of water resources [14]. World Health Organization (WHO) reported

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that in developing countries over three million people (90 % are children under 5) die every year because of waterborne diseases. Access to safe drinking water remains an urgent necessity, as 30 % of urban and 90 % of the rural Indian population still depends completely on untreated surface or groundwater resources [15]. Access to drinking water in India has increased over the past few decades with the tremendous adverse impact of unsafe water for health [16] Scarcity of clean and potable drinking water has emerged in recent years as one of the most serious developmental issues in many parts of West Bengal, Jharkahnd, Orissa, Western Uttar Pradesh, Andhra Pradesh, Rajasthan and Punjab [17] Thus, proper assessment and reporting of groundwater quality is an important issue. In the present work attempts have been made to detect groundwater quality for drinking uses.

II. MATERIALS AND METHODS

STUDY AREA

Geographically the district Varanasi is situated at 25⁰18' of Northern latitude, 83⁰ 03' of Eastern longitude and at an altitude of 128.83 m above the mean sea level in the Indo-Gangatic plain of eastern Uttar Pradesh. The mean annual precipitation is 1100 mm. The mean relative humidity of this area is about 68% with maximum 82% and minimum 30% during July to September and April to early June, respectively. The minimum and maximum average temperature of the area range from 4.4⁰C to 28.2⁰C, respectively.

SAMPLING AND ANALYSIS

Forty two groundwater samples were collected from some villages of four blocks from Varanasi District, Uttar Pradesh after the South - West monsoon. The Location map and Global Position of study areas will be show in figure 1 and table 1 respectively. The samples were collected from well, shallow hand pump and deep hand pump in area of high intensity cropping system where, the long history of phosphatic fertilizer application which is extensively used for drinking purposes. Water samples are collected in clean plastic bottles of 500 mL capacity bottles are soaked in 1:1 diluted HCl solution for 24 hours, washed with distilled water, and are washed again prior to each sampling the filtrates of sample and immediately transported to the laboratory where they stored at 4°C until analysis. The water samples were analyzed at the Soil and Water Testing Laboratory of the Department of Soil Science and Agricultural Chemistry, Institute of Agricultural Sciences, Banaras Hindu University, Varanasi. For All samples, electrical conductivity (EC) and pH values were obtained using EC and pH meters (ELICO).The parameters analyzed include the major ions sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), chloride (Cl⁻), sulphate (SO₄²⁻), carbonate (CO₃²⁻), bicarbonate (HCO₃⁻) and fluoride (F) Total dissolved solids (TDS), which were computed by multiplying the EC with a factor (EC X 640) that depend on the relative concentrations of ions. Total alkalinity (TA), CO₃ and HCO₃ were estimated by titrating with HCl. Total hardness (TH), Calcium (Ca), and Magnesium (Mg) were analyzed titrimetrically using standard EDTA; Sodium (Na⁺) and Potassium (K⁺) were measured by flame photometry; chloride (Cl) was estimated by standard AgNO₃ titration; sulphate (SO₄²⁻) was analyzed by spectrophotometer; fluoride (F) concentrations in mgL⁻¹ in groundwater samples is determined using Ion Selective Electrode Meter (Orion 96-09 model, Thermo electron Corporation).

III. METHOD OF FLUORIDE ANALYSIS

Fluoride content in water was determined electrochemically, using the direct ion sensitive electrode meter method. In this method, 25 mL of water sample and 25 mL of the TISAB solution (total ionic strength adjustment buffer which prepared 58 ml of glacial acetic acid and 12g of sodium citrate were added to 300 mL distilled water and pH of the solution was adjusted to 5.2 using 6N sodium hydroxide and then cools and diluted to 1000 mL.) were taken in a 100 mL plastic beaker. The ratio of aliquot and TISAB Solution should be 1:1.

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IV. RESULTS AND DISCUSSION

MAJOR IONS CHEMISTRY AND DRINKING WATER QUALITY

The pH value of the groundwater samples ranged from 7.6 to 8.9 with an average value 8.4 which indicates that the groundwater are alkaline in nature, but well within the limits prescribed by [18] and [19] 8.50. Electrical conductivity (EC) tells about the conducting capacity of water which in turn is determined by the presence of dissolved ions. Higher the ionisable solids, greater will be the EC. EC is a measure of total dissolved solids (TDS) i.e. - it depend upon the ionic strength of the solution. Increase in the concentration of dissolved solids, increases the ionic strength of the solution. The measured EC of the groundwater in the study area varies from 254 to 944 $\mu\text{S cm}^{-1}$ with an average value of 627 $\mu\text{S cm}^{-1}$. Concentration of total dissolved solids (TDS) in the groundwater of the study area ranged from 162 to 604 mg L^{-1} with an average value of 403 mg L^{-1} (Table 2). Water can be classified in to fresh ($\text{TDS} < 1,000 \text{ mg L}^{-1}$), brackish ($> 1,000 \text{ mg L}^{-1}$), saline ($> 10,000 \text{ mg L}^{-1}$) and brine ($1,00,000 \text{ mg L}^{-1}$) categories on the basis of TDS concentration [20]. Based on this classification the groundwater samples of the study area belong to fresh "fresh environment" and all groundwater evaluated is therefore suitable for drinking purposes. The order of dominance of the cations of the study area is $\text{Na} > \text{Mg} > \text{Ca} > \text{K}$ and of the anions is $\text{HCO}_3 > \text{Cl} > \text{CO}_3 > \text{SO}_4 > \text{Fluoride}$. Ca ranges from 18 to 80 mg L^{-1} and Mg ranges from 22 to 283 mg L^{-1} . Na concentration of the study area varies from 131 to 695 mg L^{-1} and K values range from 4 to 105 mg L^{-1} . HCO_3 is the dominant anion, which ranges from 146 to 444 mg L^{-1} , Cl content is in the range of 11 to 170 mg L^{-1} , CO_3 ranges from 12 to 66 mg L^{-1} , SO_4 ranges 3.5 to 46.6 and fluoride range from 11 to 4.63.

SUITABILITY OF GROUNDWATER FOR DRINKING AND DOMESTIC USE

The physical and chemical parameters of the analytical results of groundwater were compared with the standard guideline values recommended by the World Health Organization (WHO, 1993) and Bureau of Indian Standards [21] for drinking and public health standards (Table 1). The pH of the groundwater samples (7.6–8.9) are within the safe limit of 6.5–8.5, prescribed for drinking water. The values of TDS exceed the desirable limit of 500 mg L^{-1} in 21.42 % of groundwater samples. The total hardness (TH) is the properties of water by which it prevents the lather formation with soap and increasing the boiling point of water. Hardness of the water is the property attributed to the presence of alkaline earths. Water can be classified into soft (75 mg L^{-1}), moderately hard (75–150 mg L^{-1}), hard (150–300 mg L^{-1}) and very hard ($> 300 \text{ mg L}^{-1}$) based on hardness (Sawyer and McCarty, 1967). The total hardness of the analyzed groundwater of the study area varies between 216 and 1236 mg L^{-1} (average 707 mg L^{-1}) indicating moderately hard to very hard types of groundwater. The analytical data indicate that 57.14 % groundwater samples are come under moderately hard to very hard. The higher hardness may cause encrustation on water supply distribution systems. There is some suggestive evidence that long term consumption of extremely hard water might lead to an increased incidence of urolithiasis, anencephaly, parental mortality, some types of cancer and cardio-vascular disorders [22][23]. Concentrations of Cl^- and SO_4^{2-} are well within the desirable limit mg L^{-1} . The fluoride is beneficial to certain extent when present in the concentration of 0.8 to 1.0 mg L^{-1} for classification of dental enamel especially for children below 8 years [24] where as causes dental fluorosis if present in excess of 1.5 mg L^{-1} and skeletal fluorosis beyond 3.0 mg L^{-1} if water consumed for a prolong period i.e. 6 months to several years [25]. Higher fluoride concentration causes dental and skeletal fluorosis such as mottling of teeth, deformation of ligaments and bending of spinal cord (Tiwari and Singh 2014). The analytical data of fluoride indicate that 23.80% of groundwater samples had crossed maximum permissible limit of 1.5 mg L^{-1} prescribed by (WHO 1997, BIS 2003). Concentration of Ca^{2+} and Mg^{2+} are exceeding the desirable limits of 75 mg L^{-1} and 30 mg L^{-1} in 11.90 % and 14.28 % of the groundwater samples respectively. However, concentrations of both these ions are within the maximum permissible limit of 200 mg L^{-1} and 100 mg L^{-1} [26]. Sodium and potassium are the most important elements occurring naturally. A higher sodium intake may cause hypertension, congenital heart diseases and kidney problems [27] and the excess amount of potassium present in the water sample may lead nervous and digestive disorder [28]. The recommended permissible limit for sodium and potassium concentration in drinking water is 200 mg L^{-1} [29]. Concentrations of K^+ are within the recommended limit of 200 mg L^{-1} . However concentrations of Na^+ exceed 85.71 % of water samples of Maximum permissible limit 200 mg L^{-1} . [30]

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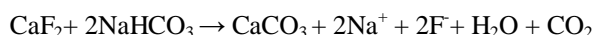
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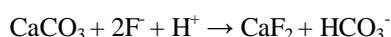
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FLUORIDE GEOCHEMISTRY

The rock porphyritic granite gneissic which contain considerable amounts of fluorite minerals especially Fluor-apatite and biotite mica, form the source of fluoride ions to the percolating groundwater. Fluorite (CaF_2) has been generally considered as source of groundwater fluoride, especially in granitic terrains [31]. However, its dissolution in freshwater is low and, furthermore, its dissolution rate is remarkably slow [32] When groundwater reacts with granite gneissic rocks for a prolonged period, the fluoride concentrations are continuously enriched, even after the groundwater reaches an equilibrium state with respect to fluorite (CaF_2) due to the removal of Ca^{2+} by precipitation of calcite (CaCO_3). Sodium carbonate type water (NaHCO_3) in weathered rock formations allows precipitation of calcite from Ca^{2+} and CO_3^{2-} ions and accelerates the dissolution of CaF_2 , thereby releasing fluoride into the groundwater as follow equation [33]



In an acidic medium fluoride is adsorbed in clays; however, in an alkaline medium, it is desorbed and thus alkaline pH is more favorable for fluoride [34]. It is clear that, if the pH is constant, the activity of fluoride is directly proportional to the amount of HCO_3^- . This relationship is independent of Ca because of the low solubility product CaF_2 . A positive correlation is observed between HCO_3^- and fluoride. Groundwater in contact with calcite and fluorite solid phases develops equilibrium reactions. The saturation of groundwater with respect to calcite and fluorite is explained as following[35] EURO, 1973).



Interpretation of hydro chemical analysis of groundwater samples reveals that the groundwater in Varanasi is within the class of excellent to good based on TDS with reference to water class, soft to hard base on total hardness and fresh with regards to the nature of groundwater based on TDS.

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Table 1. Location and global position of groundwater samples of Varanasi

S. No.	Location	Global Position	S. No.	Location	Global Position
1	Pura	N24 ⁰ 15.039' E 83 ⁰ 54.081'	22	Deura	N 24 ⁰ 24.538' E 83 ⁰ 53.112'
2	Raghunathpur	N24 ⁰ 15.039' E 83 ⁰ 54.081'	23	Deura	N24 ⁰ 24.433 ' E 83 ⁰ 52.936'
3	Pura	N 24 ⁰ 14.926' E 83 ⁰ 53.282'	24	Kashipur	N 24 ⁰ 24.590' E 83 ⁰ 52.988'
4	Raghunathpur	N 24 ⁰ 14.994' E 83 ⁰ 53.315'	25	Kashipur	N 24 ⁰ 24.259 'E 83 ⁰ 52.676'
5	Raghunathpur	N 24 ⁰ 14.879' E 83 ⁰ 53.321'	26	Kashipur	N 24 ⁰ 24.578 'E 83 ⁰ 52.978'
6	Raghunathpur	N 24 ⁰ 14.932 'E 83 ⁰ 42.901'	27	Gaura	N 24 ⁰ 25.278' E 83 ⁰ 51.678'
7	Sagunaha	N 24 ⁰ 14.816 'E 83 ⁰ 52.419'	28	Gaura	N 24 ⁰ 25.647' E 83 ⁰ 51.223'
8	Sehmalpur	N 24 ⁰ 27.636 'E 83 ⁰ 50.727'	29	Gaura	N 24 ⁰ 14.221 'E 83 ⁰ 52.110'
9	Sehmalpur	N 24 ⁰ 27.737' E 83 ⁰ 50.302'	30	Gaura	N 24 ⁰ 14.918' E 83 ⁰ 52.313'
10	Sehmalpur	N 24 ⁰ 27.767 'E 83 ⁰ 50.411'	31	Pura Raghunathpur	N 24 ⁰ 15.069'E

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11	Sehmalpur	N 24 ⁰ 27.678 'E 83 ⁰ 51.179'	32	Pura Raghunathpur	83 ⁰ 54.181' N 24 ⁰ 14.239' E 83 ⁰ 53.481'
12	Bhatauli	N 24 ⁰ 27.676' E 83 ⁰ 51.312'	33	Raghunathpur	N 24 ⁰ 14.894 'E 83 ⁰ 53.415'
13	Awashanpur	N 24 ⁰ 16.379 'E 83 ⁰ 56.176'	34	Raghunathpur	N 24 ⁰ 14.779 'E 83 ⁰ 53.221'
14	Awashanpur	N 24 ⁰ 14.932' E 83 ⁰ 42.901'	35	Sagunaha	N 24 ⁰ 14.616' E 83 ⁰ 52.619'
15	Ghamahapur	N 24 ⁰ 27.767' E 83 ⁰ 54.419'	36	Bhatauli	N 24 ⁰ 27.69 'E 83 ⁰ 52.512'
16	Dharmalpur	N 24 ⁰ 24.282' E 83 ⁰ 52.120'	37	Bhatauli	N 24 ⁰ 27.66' E 83 ⁰ 50.612'
17	Dharmalpur	N 24 ⁰ 24.220 'E 83 ⁰ 52.089'	38	Gaura	N 24 ⁰ 14.718 'E 83 ⁰ 51.313'
18	Dharmalpur	N 24 ⁰ 24.179 'E 83 ⁰ 52.147'	39	Kashipur	N 24 ⁰ 24.359' E 83 ⁰ 51.576'
19	Sahapur	N 24 ⁰ 25.734 'E83 ⁰ 250719'	40	Kashipur	N 24 ⁰ 24.269' E 83 ⁰ 51.476'
20	Sahapur	N 24 ⁰ 25.994 'E 83 ⁰ 50.362'	41	Gaura	N 24 ⁰ 14.918' E 83 ⁰ 52.313'
21	Sahapur	N 24 ⁰ 25.694 'E 83 ⁰ 50.462'	42	Gaura	N24 ⁰ 14.918' E 83 ⁰ 52.313'

Table 2. Statistics of Chemical Compositions of Major Hydro Geochemical Facies

Chemical parameters	Units	Range (mgL ⁻¹)		Mean	SD	CV
		Minimum	Maximum			
pH	-	7.6	8.9	8.4	0.290	3.45
EC	(μS/cm)	254	944	627	21.60	3.44
Ca ²⁺	(mgL ⁻¹)	18	80	44	1.50	3.41
Mg ²⁺	(mgL ⁻¹)	22	283	145	4.97	3.43
K ⁺	(mgL ⁻¹)	4	105	39	1.32	3.38
Na ⁺	(mgL ⁻¹)	131	695	397	13.59	3.42
CO ₃ ⁻	(mgL ⁻¹)	12	66	34	1.77	5.21
HCO ₃ ⁻	(mgL ⁻¹)	146	444	252	8.64	3.43
Cl ⁻	(mgL ⁻¹)	11	170	47	1.61	3.43
SO ₄ ⁻	(mgL ⁻¹)	3.5	46.6	15.4	0.52	3.38
Fluoride	(mgL ⁻¹)	0.11	4.63	1.29	0.444	34.42
TDS	(mgL ⁻¹)	162	604	401	13.59	3.38
TH	(mgL ⁻¹)	216	1236	707	24.25	3.42

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Table 3. Comparison of groundwater samples with BIS (2003) and WHO (1993) standards

Parameters	Unit	BIS (2003)		WHO (1993)		Percentage of samples above the maximum permissible limit
		Highest desirable limit	Maximum permissible limit	Highest desirable limit	Maximum permissible limit	
pH	-	6.5–8.5	6.5–9.2	6.5–8.5	6.5–9.2	Nil
TH	(mgL ⁻¹)	300	600	100	500	57.14
TDS	(mgL ⁻¹)	-	500	-	-	
Ca ²⁺	(mgL ⁻¹)	75	200	75	200	11.90
Mg ²⁺	(mgL ⁻¹)	30	100	50	150	71.42
Na ⁺	(mgL ⁻¹)	-	-	-	200	88.05
K ⁺	(mgL ⁻¹)	-	-	-	200	85.71
Cl ⁻	(mgL ⁻¹)	250	1000	200	600	Nil
F ⁻	(mgL ⁻¹)	0.6-0.9	1.5	-	-	23.80
SO ₄ ²⁻	(mgL ⁻¹)	150	400	200	400	Nil

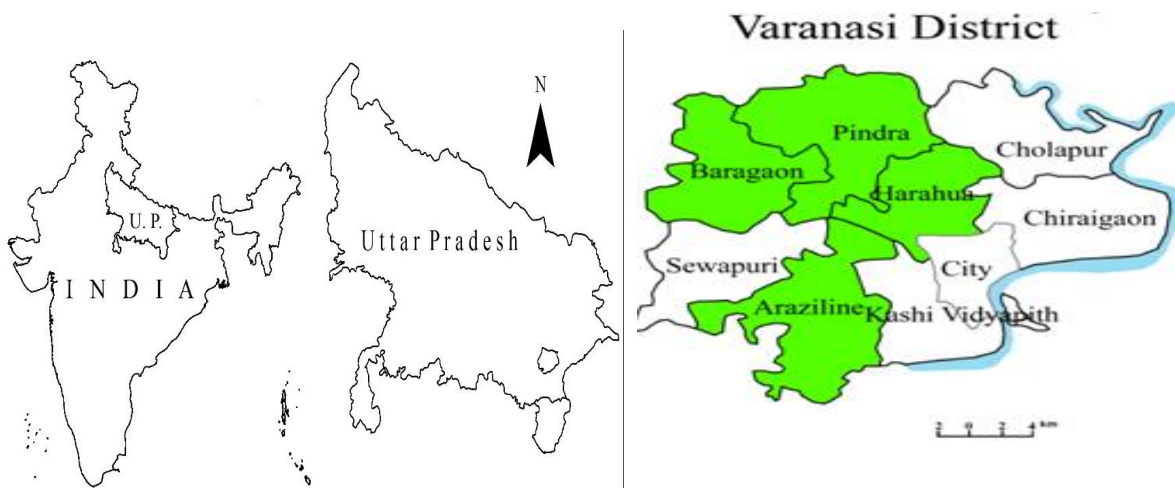


Fig: 1 Geographical Representation of Study Area