

1 **Hydrogeochemistry of intermittent alluvial aquifers controlling arsenic and**  
2 **fluoride contamination for corresponding influencing health risk**  
3 **assessment**

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## 22 **Abstract**

23 Identification and management of safe groundwater supply in a high *As* and  $F^-$  contaminated  
24 region is a major concern facing most of the developing countries worldwide. This study  
25 provides a comprehensive hydrogeochemistry result for a complex hydro-stratigraphy soil  
26 aquifer, which is bound between the Shillong plateau and Himalayan ranges in the North-  
27 Eastern region of India. In this study, distinct contaminated regions of *As* and  $F^-$  were identified  
28 in rainy (n=94) and winter (n=50) seasons groundwater samples. The maximum dissolved  
29 concentration of *As* was measured as  $71 \mu\text{g L}^{-1}$  in rainy and  $211 \mu\text{g L}^{-1}$  in winter season  
30 groundwater samples, whereas maximum  $F^-$  concentration was measured as  $7 \text{mg L}^{-1}$  in rainy  
31 and  $6 \text{mg L}^{-1}$  in winter season groundwater samples. Identified minerals saturation condition,  
32 weathering, and dissolution results of hydrogeochemistry were well corroborated with the  
33 Bivariate plot, Gibbs and Pourbaix diagrams. Results of health risk assessment showed that  
34 population of age below 18 years old are prone to carcinogenic diseases and symptoms of non-  
35 carcinogenic health risk due to daily consumption of *As* contaminated groundwater. Children  
36 of age below 18 years old, in total 39% (i.e. 6834) and 64% (i.e. 13937) were found more  
37 susceptible to arsenic ingestion effect. The male population was found prone to *As* cancer risk  
38 than the female population. Overall, this study provides a critical result about the cause of high  
39 *As* and  $F^-$  concentration in groundwater and health risk assessment, it provides a prime concern  
40 matter for the young generation which is at higher risk of *As* cancer.

41 **Keywords:** Arsenic; Hydro-geochemistry; Groundwater; water quality index, health risk  
42 assessment; Brahmaputra Flood Plain

## 43 **1 Introduction**

44 Shallow depth groundwater aquifers contaminated by arsenic (*As*) and fluoride (*F*) in  
45 alluvial aquifer is a major concern for endemic diseases of arsenicosis and fluorosis due to

46 daily water usage in most of the developing countries (Fendorf S 2010; Wen et al., 2013).  
47 Growing urban population and industrial development in South-Asian countries like India,  
48 China, Sri Lanka Bangladesh, Nepal, Vietnam, Bhutan, Pakistan etc. are primarily dependent  
49 on shallow aquifer groundwater for drinking, irrigation, domestic purposes (Mandal and  
50 Suzuki 2002; Nordstrom 2002; Schaefer et al., 2017). Alluvial groundwater aquifer (i.e.  
51 Holocene Age) of Brahmaputra river basin are known for severely affected by high dissolved  
52 concentration of As and F in the world (Enmark and Nordborg 2007; Goswami et al., 2014;  
53 Mukherjee et al., 2015; Mahanta et al., 2015; Mahanta et al., 2016; Kumar et al., 2016; Sathe  
54 et al., 2016; Sathe et al., 2018; Sathe and Mahanta 2019a; Sathe 2019b; Sathe et al., 2020).  
55 Elevated concentration of As (i.e. more than  $10 \mu\text{g L}^{-1}$  as guided by WHO permissible limit for  
56 drinking water) in the groundwater has earlier reported by Singh 2004, subsequently other  
57 researchers have validated and checked different hypothesis for the cause of high As and F in  
58 Brahmaputra flood plain (Smedley and Kinniburgh 2002; Goswami et al., 2014; Mukherjee et  
59 al., 2015; Mahanta et al. 2015; Patel et al., 2017). Goswami et al., 2014 have conducted health  
60 study on Majuli river island of the Brahmaputra river, where they measured mean As  
61 concentration in urine, hair and nail samples of local people as  $158 \mu\text{g L}^{-1}$ ,  $1223 \mu\text{g L}^{-1}$  and  
62  $2507 \mu\text{g kg}^{-1}$  respectively.

63 Indiscriminate use of Brahmaputra river and its tributaries like the Bharalu river as  
64 pathway for sewerage and industrial waste carrier has made the Brahmaputra river water unsafe  
65 for drinking and domestic usage in the Guwahati city. In early 1970s, demand for safe and  
66 sufficient water source have encourage people to use the shallow aquifer groundwater for daily  
67 usage (Mukherjee et al., 2007). Consequently, several water supply schemes such as roadside  
68 public hand pumps for limited families (i.e. around 50 family) and pipe water supply schemes  
69 for around 1000 families were installed by government organizations for the urban and village  
70 people (Enmark and Nordborg 2007; Mahanta et al. 2015).

71 Drinking contaminated groundwater with high dissolved concentration of As have resulted  
72 in severe chronic health effects, such as hyperpigmentation, keratosis, abnormalities since birth  
73 and miscarriages, circulatory, neurological and behavioural disorders, premature hair greying,  
74 respiratory complications, etc. and ultimately death due to As cancer (WHO 1993; Gebel 2000;  
75 National Academy Press 2001). High As concentration in groundwater reported from  
76 Brahmaputra flood plain is  $606 \mu\text{g L}^{-1}$  (Mahanta et al., 2015) whereas in alluvial aquifer sand  
77 it was measured as  $61 \mu\text{g kg}^{-1}$  (Sathe and Mahanta 2019a). Concentration of As (up to  $0.22 \text{ mg}$   
78  $\text{kg}^{-1}$ ) in phosphate fertilizers were reported as a major anthropogenic source near agricultural  
79 land.

80 Population affected by fluorosis are observed mainly from tropical countries like India,  
81 China, Japan, Sri Lanka, Pakistan, Turkey, Korea, Italy, Brazil (Srinivasa Rao, 1997; Brindha  
82 et al., 2011). Symptoms of high  $\text{F}^{-}$  concentration groundwater consumption observed are bone  
83 fluorosis and crippling bone, mostly found in human aged below 10 years due to prolonged  
84 exposure to high  $\text{F}^{-}$  concentrations (Yadav et al. 2019). The toxic effect of  $\text{F}^{-}$  depends on age,  
85 duration and immune system of person (Amalraj and Pius 2013). The other harmful effects  
86 reported due to high  $\text{F}^{-}$  ingestion are a decrease in blood cells, osteoporosis, genetic damage  
87 decrease thyroid function, mental retardation, hypertension, depression, impairment of nervous  
88 system, premature aging, cancer and renal disease etc. (Hillier et al. 1996; Hurtado and  
89 Tiemann 2000; Susheela et al. 2005; Xiong et al. 2007; Valdez-Jiménez et al. 2011; Sun et al.  
90 2013; Jiang et al. 2019). Daily intake of  $\text{F}^{-}$  within the permissible limit is beneficial to health  
91 and it protect from decaying of tooth from enamel to the tooth, also it helps in formation of  
92 new bones (Adimalla and Venkatayogi 2017; Dehbandi et al. 2018). The major concern for  
93 safe drinking water to authorities of developed countries is to maintain the desirable  
94 concentration of  $\text{F}^{-}$  in drinking water (Jones et al. 2005; Petersen and Lennon 2004; Podgorny  
95 and McLaren 2015).

96 In different regions of Brahmaputra flood plain, broad consensus was As mobilized into  
97 shallow aquifer groundwater is desorption and reductive dissolution of Fe oxy/hydroxide  
98 minerals and groundwater fluctuation (Smedley and Kinniburgh 2002; Mahanta et al. 2015;  
99 Sathe et al. 2019a). Few studies have presented the results on mobilization mechanisms and  
100 mitigation strategies for the groundwater As and F<sup>-</sup> contamination problem in Brahmaputra  
101 flood plain (van Geen et al., 2008a; van Geen et al., 2008b; Mukherjee et al., 2015; Sathe et  
102 al., 2015). Brindha et al. (2011) have reported that dissolved fluoride concentration in  
103 groundwater may increases due to evaporation groundwater from the shallow aquifer may be  
104 affected by lowering of groundwater table in summer season in India. Groundwater table in  
105 Brahmaputra flood plain found at a depth of 5 to 10m from ground surface and groundwater  
106 table fluctuation was observed at in between 3 to 5m (Mahanta et al., 2015; Sathe and Mahanta  
107 2019). Such long-time residual time of groundwater with the aquifer material favour for the  
108 soil-water interaction and dissolve the fluoride in different groundwater pH conditions.  
109 Publication on health risk assessment on this area was vague and less studies have reported on  
110 the risk of consumption of groundwater and total people are at the risk of fluorosis in  
111 Brahmaputra flood plain.

112 The detailed mineralogical studies by XRD, morphological studies, and saturation indices  
113 (SI) have reported that the primary As and F bearing minerals were found to be the cause for  
114 high concentration in the Brahmaputra flood plain (Sathe et al., 2018; Sathe and Mahanta  
115 2019a). The statistical analysis, Pourbaix diagram, Gibbs plot, and minerals saturation indices  
116 were helped to identify geochemical mechanisms and harmful metal species prevailing in the  
117 groundwater samples. Groundwater quality index study further assisted to identify  
118 appropriateness for various usage such as drinking, agriculture and industry (Kamboj &  
119 Kamboj 2019).

120 The carcinogenic health risk assessment provides a probable number of peoples who are  
121 at the risk of ingestion and dermal effects of As contaminated groundwater sources (USEPA,  
122 2012; Singh and Ghosh 2012). Table 1 shows concentration of As and F<sup>-</sup> in groundwater and  
123 river water measured in different countries and methods adopted for health risk assessment.  
124 Few studies have conducted on health survey and measured concentration in the human body  
125 for the north eastern states of India (Goswami et al., 2014). Understanding of spatial  
126 distribution of chemical species by ordinary kriging method provides are occurring health risk  
127 in the region and concentration variation pattern in the study area. The contour gradient of  
128 kriging method helps to understand the direction of groundwater flow and predict future  
129 contaminated region in the study area (Sathe and Mahanta 2019a). Schuh et al. (1997) found  
130 that increasing trends in the groundwater aquifer for a particular solute were mainly caused by  
131 recharge or infiltration from surface water bodies and partially controlled by anthropogenic  
132 activities such as heavy pumping by irrigation well and community water supply wells in that  
133 study area. Mukherjee et al., 2007 in West Bengal region and Sathe and Mahanta 2019a study  
134 in Brahmaputra flood plain have observed that depth wise distribution of dissolved As  
135 concentration in alluvial aquifers can be influenced by heavy groundwater pumping from the  
136 deeper aquifer.

137 In north-eastern flood plain region of India mainly the Brahmaputra flood plain (Assam),  
138 studies were focused on the identification of As and F<sup>-</sup> sources, mobilization mechanisms, and  
139 severely affected regions were reported. This study was aimed to find 1) suitability of  
140 groundwater usage determined by water quality index, 2) identify primary and secondary As  
141 and F<sup>-</sup> minerals in the alluvial aquifer, 3) carcinogenic health risk assessment and 4) understand  
142 the concentration gradient, delineate safe aquifer and low risk region for drinking water.

## 143 2 Study area

144 North-Eastern region of India mainly comprises eight states. The Guwahati city of Assam  
145 state has vital importance in terms of its industrial growth, agricultural fertile land and road  
146 connectivity. The study area is situated between a longitude of E 91.4666° to E 91.8868° and  
147 latitude N 26.2061° to N 26.0520° on the southern part of state Assam, it covers an area of  
148 328 km<sup>2</sup> (Figure 1). Total population of city is 1,116,267 and population density as 3,400/km<sup>2</sup>  
149 in Guwahati city (Population of Guwahati 2020). Guwahati city is growing from the foothills  
150 of the Shillong plateau. Outskirts of Guwahati city is occupied by industrial areas, government  
151 offices, colleges, schools, and the central part is densely populated with a residential building  
152 and shopping malls.

153 Bharalu River is one of the tributaries of Brahmaputra river, it originates in the Khasi Hills  
154 of Meghalaya flows through the centre of the Guwahati city and confluence with the  
155 Brahmaputra river on the northern side of the city (Figure 1). This tributary river has vital  
156 importance in terms of water and sewage water carry from the city. Guwahati city receives an  
157 annual rainfall of 1,752 mm (IMD Guwahati 2020). Most of the people in city uses groundwater  
158 as a source for drinking and domestic purposes in the city. The groundwater supply tubes are  
159 usually installed at a depth of 100 ft. to 150 ft. whereas government tube wells are usually  
160 installed below 250 ft. to 1000 ft. depth.

## 161 3 Materials and method

### 162 3.1 Groundwater sampling

163 For rainy season, groundwater samples were collected in such a way that it covers the  
164 entire Guwahati city, whereas in the winter season, high dissolved concentration of As and F<sup>-</sup>  
165 areas were mainly targeted to understand the concentration variation in different seasons. For  
166 the rainy season, 94 groundwater sample and in the winter season, 50 groundwater samples

167 were collected in a month of November 2019 and in January 2020. The water samples were  
168 deliberately collected from government and private bore well sources, obligatory information  
169 for each groundwater sources (viz. private wells, hand tube wells and open well) such as screen  
170 depth, water table depth, discharge rate, installation year, number of people depend on it, water-  
171 related health issue reported since installation, and GPS coordinates (Garmin Montana 610)  
172 were collected during sampling. The stagnant groundwater (i.e. partially oxidized) was  
173 expelled out by continuous pumping for 10 minutes before sample collection from each tube  
174 wells and stored in 250 mL capacity high-density polyethylene bottles (Tarson, India).  
175 Groundwater were stored in two different sets, for cation analysis samples was acidified by  
176 adding few drops of HNO<sub>3</sub> and made its pH below 2 (1% v/v, Suprapur, Merck) and another  
177 set of non-acidified groundwater sample was collected for anion analysis. Precaution was taken  
178 during groundwater sampling and bottles filled by ensuring that there is no headspace left in  
179 the sampling bottles, bottles were stored in dark place and cold room.

### 180 **3.2 Groundwater analysis**

181 The time and temperature-dependent groundwater hydro-chemical parameters such as  
182 electrical conductivity (EC), dissolved oxygen (DO), pH, total dissolved solids (TDS),  
183 temperature (°C) and oxidation-reduction potential (ORP) were measured on-site during  
184 sampling using a multiparameter (YSI Inc. 550A, Sondes) water testing kit. Ion  
185 chromatography (M/s Metrohm, Switzerland) instrument was used to measure the selective  
186 cation and anion concentration in groundwater samples. For the analysis, Metrosep C2-250,  
187 4×250 mm column was used and operated at 20 °C. Before every groundwater sample analysis,  
188 samples were filtered through a 0.2 µm filter (Whatman, 6872-2502 GD/X 25 mm Syringe  
189 Filter, PVDF filtration medium). A mobile phase of 1 litre was prepared by adding 100 mL of  
190 pyridine dicarboxylic acid and 1.7 mL of 1M HNO<sub>3</sub> solution in 1 litre of volumetric flask. The  
191 mobile phase solution prepared for IC instrument analysis was maintained at 1 mL min<sup>-1</sup> flow



192 rate and pressure 80 MPa applied during analysis. The instrument was calibrated before  
193 analysis using multielement Ion Chromatography anion and cation standard solution (M/s  
194 Merck).

195 Arsenic concentration in groundwater samples were determined by a hydride generation  
196 atomic absorption spectrophotometer (HG-AAS, VGA-77 detection limit  $<1 \mu\text{gL}^{-1}$ )  
197 instrument. The total concentration of iron and manganese was determined by a graphite  
198 furnace atomic absorption spectrophotometer (GF-AAS, GTA-120, Varian, SpectrAA-55).  
199 The minimum concentration detection limit for Fe was  $1.5 \mu\text{g L}^{-1}$  and for Mn it was  $1.0 \mu\text{g L}^{-1}$   
200 (Sathe et al., 2018).

### 201 3.3 Speciation modelling

202 The minerals saturation Indices (SI) for predominant minerals were calculated using  
203 Visual MINTEQ 3.1 software using groundwater hydrogeochemistry results in following Eq.  
204 (1) Gustafsson, 2014):

205  $Saturation\ Indices (SI) = \log(IAP \times KT) \dots$  equation (1)

206 whereas ion activity product is abbreviated as 'IAP' and 'KT' represents at ambient  
207 temperature, equilibrium solubility constant for particular mineral. Thermodynamic database  
208 present in software (i.e. thermo. vdb) was used for the determination of respective minerals  
209 'SI' values. The 'SI' for minerals possessing positive, zero, and negative values have suggested  
210 that these minerals are thermodynamically supersaturated, equilibrium, and unsaturated  
211 respectively. Redox coupling was assigned mainly for  $\text{As}^{+3} / \text{As}^{+5}$ ,  $\text{Fe}^{+2} / \text{Fe}^{+3}$  and  $\text{Mn}^{+2} / \text{Mn}^{+3}$   
212 metal species.

### 213 3.4 Ordinary kriging

214 Kriging is a stochastic method commonly applied for spatial data interpolation which  
215 provide the possible values of particular solute at unsampled sites. For present study, to  
216 understand the spatial concentration variation of Mn, F<sup>-</sup>, Fe, and As in different depths of  
217 aquifer, ordinary kriging method with combination of variogram method were applied. In this  
218 method, the measured surrounding values were used directly in the empirical mathematical  
219 formulas, which provide intermittent spatial data in terms of contour values for the delineated  
220 study area. The ordinary kriging method assumes the constant mean as unknown, this method  
221 is more relevant when there is a spatial correlation in distance and directional bias in the  
222 analysed data. Ordinary kriging method often practiced in geology and agricultural department  
223 for understanding variability of soil strata (Oliver and Webster 1990). The optimum values for  
224 range, sill, nugget, azimuth-angle, contribution, dip-angle, and plunge-angle were used in such  
225 a way that it can accommodate minimum and maximum distance sample location for empirical  
226 semi-variogram model of Spherical, Exponential, Gaussian analysis. The applied empirical  
227 semi-variogram model provides an information on the spatial autocorrelation of datasets.

228 Groundwater modelling software i.e. GMS 10.2 was used by considering anisotropy of  
229 for spatial and vertical distribution (i.e. three-dimensional) of aquifer material for As, Fe, F<sup>-</sup>,  
230 and Mn distribution analysis. In kriging method, values in between were determined by  
231 assuming that over a region's values varied continuously (Deutsch and Journel, 1992). The  
232 ordinary kriging method solves the following equations;

$$233 \gamma(\bar{x}, \bar{y}) = \frac{1}{2N} \times \sum (Z(\bar{x}) - Z(\bar{y}))^2 \dots \text{equation (2)}$$

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

237  $Z(\bar{x}_o) = \sum_{i=1}^N \lambda_i \times Z(\bar{x}_i) \dots$  equation (3)

238 where the estimated and observed values at point  $\bar{x}_o$  is  $Z(\bar{x}_o)$  and at 'i<sup>th</sup>' point  $\bar{x}_i$  is  $Z(\bar{x}_i)$ .

239 Observed value in the ' $\lambda_i$ ' point is the weight of  $\bar{x}_i$  and 'N' is the total number of observed  
 240 points. Following semi-variogram models such as exponential, theoretical spherical, and  
 241 gaussian were used for the kriging method.

242 Spherical model;

243  $\gamma(h) = C_o + C \left[ 1.5 \left( \frac{h}{a} \right) - 0.5 \left( \frac{h}{a} \right)^3 \right] \quad h \leq a \quad \dots$  equation (4)

244  $\therefore C_o + C \quad h > a$

245 Exponential model;

246  $\gamma(h) = C_o + C \left[ 1 - \exp \left( -\frac{3h}{a} \right) \right] \dots$  equation (5)

247 Gaussian model;

248  $\gamma(h) = C_o + C \left[ 1 - \exp \left[ -\left( \frac{3h}{a} \right)^2 \right] \right] \dots$  equation (6)

249 where ' $C_o$ ' is the nugget effect; ' $C$ ' is the sill; and ' $a$ ' is the range. The spatial data required  
 250 for semi-variogram models provided by theoretical semi-variogram model used in these  
 251 analyses.

### 252 3.5 Weighted arithmetical water quality index (WQI)

253 To classify the groundwater quality WQI method was followed. This a common method  
 254 usually used by hydrogeochemistry experts (Chauhan and Singh 2010; Chowdhury et al., 2012)  
 255 for the decision-making policy and followed WQI equation (Rown et al., 1972) for the  
 256 calculation:

257 
$$WQI = \frac{\sum Q_i W_i}{\sum W_i} \dots \text{equation (7)}$$

258 For each parameter, using following equation a quality rating scale i.e. ‘Q<sub>i</sub>’ was calculated

259 
$$Q_i = 100 \times \left[ \left( \frac{V_i - V_o}{S_i - V_o} \right) \right] \dots \text{equation (8)}$$

260 Where, estimated concentration is abbreviated as ‘V<sub>i</sub>’ for ‘i<sup>th</sup>’ parameter, is abbreviated as  
 261 ‘V<sub>o</sub>’ for pure water. The standard recommended value i.e. ‘S<sub>i</sub>’ for ‘i<sup>th</sup>’ parameter, ideal pure  
 262 water is ‘V<sub>o</sub>’ = 0 (except pH =7.0 and DO = 14.6 mg L<sup>-1</sup>)

263 The unit weight ‘W<sub>i</sub>’ for each sample was calculated by using following equation:

264 
$$W_i = \frac{K}{S_i} \dots \text{equation (9)}$$

265 Where, proportionality constant is abbreviated as ‘K’ and calculated using following  
 266 equation:

267 
$$K = \frac{1}{\sum \left( \frac{1}{S_i} \right)} \dots \text{equation (10)}$$

268 Obtained WQI values were categorized into five grades (i.e. A to E) and rated for each  
 269 groundwater samples. The WQI values laid in between 0 to 25 was categorized in “Grade – A”  
 270 and rated as “Excellent water quality” which suggest that it is safe for drinking purposes. The  
 271 WQI value between 26 to 50 is rated as “Good water quality” and graded in the “B” category.  
 272 The third category is “Grade-C” and rated as “Poor water quality” for WQI values laid between  
 273 51 to 75. The “Grade- D” category water rated as “Very poor water quality” for WQI values  
 274 laid between 76 to 100. The WQI values above 100 is graded as “E” and rated as “Unsuitable  
 275 for drinking purpose”.

### 276 3.6 Carcinogenic health risk assessment (CHA)

277 Carcinogenic health risk assessment posed by drinking groundwater with high dissolved  
278 concentration of As on present population was assessed by following USEPA 2004 guideline.  
279 Mainly ingestion of As and risk assessment for dermal was evaluated by using the following  
280 empirical equations (11) & (12):

$$281 \text{ADD}_{\text{Ingestion}} = \frac{(C_w \times IR \times EF \times ED)}{(B_w \times AT)} \dots \text{equation (11)}$$

$$282 \text{ADD}_{\text{Dermal}} = \frac{(SA \times EF \times C_w \times K_p \times ED \times ET \times CF)}{(AT \times BW)} \dots \text{equation (12)}$$

283 Where, heavy metals average concentration in groundwater samples is ‘ $C_w$ ’ ( $\mu\text{g L}^{-1}$ ); ‘IR’,  
284 ingestion rate ( $\text{L day}^{-1}$ ) the adopted IR values for this study was  $2.0 \text{ L day}^{-1}$  and  $0.64 \text{ L day}^{-1}$   
285 for adults and children (Xiao et al., 2019), exposure frequency is abbreviated as ‘EF’ ( $\text{days}$   
286  $\text{year}^{-1}$ ) and  $350 \text{ days year}^{-1}$  values used for the calculation (USEPA, 2004), exposure duration  
287 is abbreviated as ‘ED’, and 70 years and 6 years maximum value was adopted for the adults  
288 and children population respectively. Average body weight IS abbreviated as ‘Bw’ for the  
289 calculation, 60 kg and 15 kg maximum weight was considered for adults and children  
290 population (Njugunaet al., 2019; Saleem et al., 2019). The average exposure time is abbreviated  
291 as ‘AT’ and for the above calculation 70 years and 6 years was adopted for adults and children  
292 populations. Surface area of the skin is abbreviated as ‘SA’ whereas,  $6,600 \text{ cm}^2$  and  $18,000$   
293  $\text{cm}^2$  values used for children and adult’s population. Dermal permeability coefficient is  
294 abbreviated as ‘ $K_p$ ’ and for calculation  $0.001 \text{ cm h}^{-1}$  value adopted for As contaminant (EPA  
295 2004). ‘ET’ abbreviated for exposure time, for bathing and shower,  $0.25 \text{ h day}^{-1}$  ‘ET’ value  
296 was adopted for the calculation. ‘CF’ is a unit conversion factor,  $0.001 \text{ L cm}^{-3}$  (USEPA, 2004).  
297 According to ‘ADD<sub>ingestion</sub>’ and ‘ADD<sub>Dermal</sub>’ calculation, the values below one (i.e.  $<1$ )  
298 suggested that these groundwaters sources are safe for drinking water purposes but values  
299 above one (i.e.  $>1$ ) indicate that these groundwater sources are unsafe for drinking purposes

300 and particular the population is at the risk of early carcinogenic effect due to drinking of As  
301 contained groundwater (Njuguna et al., 2019).

## 302 **4 Results and Discussion**

### 303 **4.1 Groundwater hydrogeochemistry**

304 Groundwater quality monitoring for carcinogenic and toxic chemicals at different depth  
305 of aquifers and sources was meticulously studied in this analysis. The results of temperature  
306 and time sensitive parameters such as pH, DO and ORP for rainy season groundwater samples  
307 depict that the acidic to alkaline nature by pH (5.9 to 8.9) values, ORP results showed low (i.e.-  
308 359 mV) to high (i.e. 503 mV) reducing condition and DO results (i.e. 0.9 mg L<sup>-1</sup> to 7.8 mg L<sup>-1</sup>)  
309 in groundwater samples. Similarly, in winter season pH (viz. 6.3 to 9.3) shows near neutral  
310 to alkaline and hard water condition, ORP showed strong reducing (viz. - 498 mV to 189 mV)  
311 condition prevailing in groundwater aquifer. A common problem identified during personal  
312 interaction with the consumers was white colour scaling on inside of cooking utensils,  
313 encrustations in water supply structure and inside of water supply pipe lines.

314 The results of cation and anion analysis provides a vital information to assess the health  
315 of groundwater consumers and identify possible solution required for the study area.  
316 Groundwater temperature, DO are an important parameter which provide signs of present  
317 physicochemical process and biological activity prevailing in groundwater aquifers (Ali, Islam,  
318 & Rahman, 2016). Comparatively, in the winter season, high concentration of NO<sub>3</sub><sup>-</sup> as 25.2±  
319 3.7 mg L<sup>-1</sup> (i.e. maximum ± S.D) was found (Table 2a and 2b), which indicates excess use of  
320 pesticides on adjoining agricultural land and it consequently infiltrate into shallow depth  
321 groundwater aquifer. These anthropogenic sources of As and F<sup>-</sup> chemicals in groundwater  
322 aquifer provide a favourable condition for microbial mineralization. The measured high  
323 concentration of SO<sub>4</sub><sup>-2</sup> (82.9 ± 16.2 mg L<sup>-1</sup>) and Cl<sup>-</sup> (105 ±23.8 mg L<sup>-1</sup>) in winter season

324 groundwater samples suggest the secondary salinity source is a cause for high concentration.  
325 Compared to rainy season, the winter season groundwater results showed high concentration  
326 of  $\text{HCO}_3^-$  ( $418 \pm 63 \text{ mg L}^{-1}$ ) which indicates active weathering process of carbonaceous  
327 minerals in shallow depth aquifer. High concentration of dissolved fluoride (i.e.  $7.3 \pm 1.3 \text{ mg}$   
328  $\text{L}^{-1}$ ) was observed in the rainy season groundwater samples than winter season (i.e.  $6.1 \pm 1.3$   
329  $\text{mg L}^{-1}$ ) samples, which indicates favourable aquifer conditions for a geogenic source of  
330 fluoride bearing minerals (viz. fluorite, mica, biotite) (Chaurasia et al. 2007). The anionic  
331 analysis for the rainy season samples showed concentration wise abundance as  $\text{HCO}_3^- > \text{Cl}^- >$   
332  $\text{SO}_4^{2-} > \text{F}^- > \text{NO}_3^-$  similarly, in winter season it is measured as  $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{F}^-$  for  
333 study area groundwater samples.

334 Dominant  $\text{Na}^+$  cation concentration was measured in the rainy season groundwater sample  
335 results. The descending cation concentration order was found as  $\text{Ca}^{+2} > \text{K}^+ > \text{Mg}^{+2}$  whereas  
336 similar concentration trend was observed in winter season groundwater results, except for few  
337 samples  $\text{Mg}^{+2}$  concentration was observed high as  $12038 \text{ mg L}^{-1}$ ,  $2661 \text{ mg L}^{-1}$  and  $3912 \text{ mg}$   
338  $\text{L}^{-1}$ . There was significant concentration variation in the winter season groundwater analysis  
339 results, where more than 50% decrease in concentration of Fe was measured, which indicates  
340 that study area aquifers are prone to high aquifer flushing and dilution (Table 2a, 2b). In both  
341 seasonal groundwater sample analysis results, high dissolved  $\text{Na}^+$  concentration has indicated  
342 that alumino-silicate and/or sodium-silicate minerals weathering or dissolution process was the  
343 cause for high concentration in the study area aquifer. Similarly, high concentration of  $\text{Ca}^{+2}$   
344 indicates weathering of carbonate mineral such as gypsum, plagioclase and feldspar minerals  
345 which was a second dominant process prevailing in the groundwater aquifer (Sathe and  
346 Mahanta., 2019a). The high concentration of  $\text{Na}^+$ ,  $\text{Ca}^{+2}$ ,  $\text{K}^+$  and  $\text{Mg}^{+2}$  in groundwater analysis  
347 also indicates the influence of high cation exchange mechanism, evaporation, infiltration of

348 surface water from sewage and agriculture land, and poor drainage system in study area (Kumar  
349 et al., 2006).

#### 350 **4.2 Hydrogeochemistry of arsenic and fluoride**

351 The arsenic concentrations were measured between bdl to  $71.3 \pm 13.8 \mu\text{g L}^{-1}$  in the rainy  
352 season groundwater samples whereas for toxic arsenite [i.e. As (III)] species as it was measured  
353 in between bdl to  $9.7 \pm 2.4 \mu\text{g L}^{-1}$  in rainy season sample and comparatively low toxic arsenate  
354 [i.e. As (V)] species measured between bdl to  $212 \pm 32.8 \mu\text{g L}^{-1}$  in winter season groundwater  
355 samples. High concentration values of As in winter season samples was significantly correlated  
356 with on-site measured ORP value results which suggests that reducing groundwater aquifer  
357 favourable for dissolved arsenic concentration in the study area. Similarly, more than WHO  
358 drinking water permissible limit for Fe was measured as  $24 \pm 3.3 \text{ mg L}^{-1}$  in rainy season  
359 samples and for Mn it was measured as  $0.9 \pm 0.2 \text{ mg L}^{-1}$  and in winter season  $0.3 \pm 0.1 \text{ mg L}^{-1}$   
360 support reductive dissolution mechanism prevailing in study area aquifer. Studies have  
361 reported that high manganese in groundwater can causes low intelligence quotient in children  
362 (Khan et al., 2012). High concentration of Fe and Mn measured in rainy season samples  
363 suggested that the aquifer is under reducing condition and favourable for reductive dissolution  
364 mechanism of iron oxy/hydroxide minerals in groundwater aquifer.

365 The hydrogeochemical process such as weathering and dissolution are the dominant  
366 mechanism for high dissolved fluoride in groundwater aquifer (Saxena and Ahmed, 2003;  
367 Adimalla and Venkatayogi, 2017). Dissolution of fluorine in acidic conditions were observed  
368 due to complexes of aluminum difluoride ( $\text{AlF}_2^+$ ) and di-fluoroaluminum ( $\text{AlF}_2$ ) in  
369 groundwater (Wenzel and Blum 1992). Wenzel and Blum (1992) study have inferred that  
370 fluorine solubility increases above  $\text{pH} > 6.5$  due to repulsion of negatively charged surfaces  
371 such as clay present in groundwater bearing aquifer. Therefore, the risk of groundwater is high



372 at strong acidic ( $\text{pH} < 6$ ) as well as high alkaline ( $\text{pH} > 6.5$ ) groundwater condition (Wenzel  
373 and Blum 1992).

374 Dissolved form of fluoride is vulnerable to the ion exchange process, with hydroxyl anion  
375 because of almost equal ionic radius of  $\text{OH}^-$  (i.e.  $1.40 \text{ \AA}$ ) and  $\text{F}^-$  (i.e.  $1.36 \text{ \AA}$ ). Furthermore,  
376 dissolution and weathering of fluoride containing minerals such as muscovite, biotite,  
377 hornblende and amphibole are favourable to sodium bicarbonate dominant facies in the  
378 groundwater aquifer (Handa 1975). In piper plot predominant hydrogeochemical facies found  
379 are  $\text{Ca}^{2+}-\text{Na}^+-\text{HCO}_3^-$  and  $\text{Ca}^{2+}-\text{HCO}_3^-$  suggested that the groundwater of the study area is  
380 favourable to fluoride bearing minerals dissolution and allow precipitation of  $\text{Ca}^{2+}$  and  
381  $\text{CO}_3^{2-}$  ions in aquifer. Higher concentration of  $\text{HCO}_3^-$ ,  $\text{Na}^+$  and  $\text{pH}$  favours for the release of  $\text{F}^-$   
382 in in groundwater aquifer (Kumar et al., 2017). Ion exchange process between  $\text{Na}^+$  and  $\text{Ca}^+$  in  
383 weathered aquifer zone increases  $\text{F}^-$  concentration whereas it decreases with increasing  $\text{Ca}^+$   
384 concentration due to precipitation of  $\text{CaF}_2$  in groundwater aquifer. Thus, co-occurrence of  $\text{As}$   
385 and  $\text{F}^-$  in groundwater mainly due to desorption from  $\text{Fe}$  (hydro)-oxides and  $\text{CaF}_2$  bearing  
386 minerals surfaces (Gomez et al., 2009).

### 387 **4.3 Statistical analysis and mineral saturation indices**

388 The primary groundwater analysis results have depicted that groundwater aquifer of  
389 depth 200 ft. to 500 ft. can yield  $\text{As}$  (Figure 2a) and  $\text{F}^-$  (Figure 2b) safe groundwater. The  
390 statistical analysis by Pearson correlation method showed positive correlation value as  $\rho = 0.6$   
391 between dissolved concentration of  $\text{As}$  vs  $\text{Fe}$  for rainy season samples. It suggests significant  
392 affinity with dissolved concentration values for each other. In winter season, insignificant  
393 Pearson correlation values such as  $\rho = 0.04$  was observed between  $\text{As}$  vs.  $\text{Fe}$  (Figure 2c), it  
394 suggests that aquifers of the study area are highly susceptible for flushing capacity and  
395 vulnerable to surface water infiltration. Other Pearson correlation analysis in both the season  
396 groundwater samples for  $\text{As}$  with  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Mn}$  showed (Figure 2d, 2e and 2f),

397 insignificant correlation values, which suggests that groundwater aquifer have high hydraulic  
398 conductivity and have less residential time.

399 Hydrogeochemical facies were identified in Piper plot using GW chart software (Current  
400 Version 1.30.0) developed by USGS (Piper 1944). Piper plot includes three distinct diagrams  
401 which consists of two triangles, one for cation (i.e.  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{K}^+$  and  $\text{Na}^+$ ) and another for  
402 anion (i.e.  $\text{HCO}_3^-$ ,  $\text{SO}_4^{-2}$ ,  $\text{Cl}^-$  and  $\text{CO}_3^-$ ) whereas one diamond-shape diagram plot shows  
403 combine cation and anion facies (Sathe et al., 2018). The results of piper plot showed three  
404 dominant hydrogeochemical facies in rainy season, such as 1)  $\text{Ca}^{+2} - \text{HCO}_3^-$  2)  $\text{Ca}^{+2} - \text{Na}^+ -$   
405  $\text{HCO}_3^-$  3)  $\text{Na}^+ - \text{SO}_4^{-2} - \text{Ca}^{+2} - \text{HCO}_3^-$  whereas, in winter season major two hydrogeochemical  
406 facies mainly 1)  $\text{Ca}^{+2} - \text{HCO}_3^-$  and 2)  $\text{Ca}^{+2} - \text{Na}^+ - \text{HCO}_3^-$  were identified in groundwater samples  
407 (Figure 3). These distinct hydrogeochemical facies, indicates alkali mineral dissolution and  
408 causes alkaline and acidic nature of rainy and winter season groundwater. The high  $\text{Na}^+$   
409 concentration coupled with low  $\text{Ca}^{+2}$  concentration suggests that the cause of ion exchange  
410 process and precipitation of  $\text{CaF}_2$  in the groundwater aquifer. It suggests that the measured low  
411 concentration of  $\text{F}^-$  in respective wells groundwater samples are safe for drinking purposes in  
412 the study area. Results of hydrogeochemical facies observed in Piper plot were well supported  
413 with the previous studies results of Brahmapootra flood plain (Enmark and Nordborg 2007;  
414 Mahanta et al., 2015; Sathe et al., 2018).

415 Hydrogeochemical processes and mechanisms such as evaporation, weathering, and  
416 dissolution of minerals were identified using cation and anion concentration data in two-  
417 dimensional scatter plot for the study area. The sample concentration close to the line 1:1 in  
418 scatter plot of  $\text{SO}_4^{-2} + \text{HCO}_3^-$  versus  $\text{Ca}^{+2} + \text{Mg}^+$  (Figure 4a) indicates dissolution of minerals  
419 such as calcium and magnesium bearing gypsum, dolomite and calcite are the cause for high  
420 As and  $\text{F}^-$  concentration the groundwater aquifer (Cerling et al., 1989). Groundwater samples  
421 laid near to right side of the graph indicates that ion exchange process prevailing in the aquifer

422 samples due to excess dissolved concentration of  $\text{SO}_4^{2-} + \text{HCO}_3^-$  in groundwater (Fisher and  
423 Mulican 1997). Whereas, insignificant cation ion exchange process in groundwater samples  
424 was observed in excess concentration of  $\text{Ca}^{+2} + \text{Mg}^+$  in samples, which are laid near to the left  
425 corner in the two-dimensional scatter plot (Cerling et al., 1989). Similarly, scatter plot of  $(\text{Ca}^{+2}$   
426  $+ \text{Mg}^+) / \text{HCO}_3^-$  versus  $\text{Cl}^-$  indicates presence of  $\text{Mg}^+$  and  $\text{Ca}^{+2}$  in samples. Ratio below 1 or  
427 around 0.5 indicates  $\text{Ca}^{+2}$  and  $\text{Mg}^+$  concentration is solely added into groundwater by the  
428 dissolution and weathering of carbonates minerals also with accessory minerals such as  
429 pyroxenes and amphibole (Sami1992). Scatter plot results show that concentration of  $\text{Ca}^{+2}$  and  
430  $\text{Mg}^+$  is mainly controlled by dissolution and weathering of carbonate and amphibole minerals  
431 in the aquifer. The insignificant ion exchange process was observed in  $\text{Ca}^{+2} + \text{Mg}^+$  versus  $\text{Cl}^-$   
432 plot, its affinity with the dissolved concentration of  $\text{Ca}^{+2} + \text{Mg}^+$  and salinity was observed in  
433 both season groundwater samples (Figure 4c).

434 Gibbs diagram often shows a relationship between lithological characteristics with the  
435 subsurface groundwater composition (Gibbs 1970). The Gibbs diagram distinctly divided into  
436 three distinct regions mainly precipitation, rock and evaporation. Most of the groundwater  
437 sample of rainy and winter season were laid in the rock domain, which suggests solid-liquid  
438 interaction process (i.e. weathering and dissolution process) of  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$  bearing  
439 minerals (Figure 4d).

#### 440 **4.4 Delineation of mineral saturation aquifers**

441 The in-situ measured groundwater parameters such as pH and Eh were used to identify  
442 dominant As,  $\text{F}^-$ , Mn, and Fe species in the Pourbaix diagram (Figure 5a,5b,5c,5d). Mainly  
443 arsenate ( $\text{As}^{+3}$ ) species (i.e.  $\text{H}_x\text{AsO}_3^x$ ) higher dissolved concentration was found in rainy and  
444 winter season groundwater samples than arsenite ( $\text{As}^{+5}$ ) species (i.e.  $\text{H}_x\text{AsO}_4^x$ ) (Figure 5a). The  
445 partial oxidizing groundwater condition were observed from Pourbaix diagram. The dominant  
446 fluoride species such as fluorite was observed in figure 5b. Similarly, the manganese bearing

447 dominant minerals rhodochrosite was observed in figure 5c and iron bearing minerals such as  
448 siderite, ferrihydrite, and calcite species were identified in figure 5d from Pourbaix diagram.

449 Minerals saturation indices (SI) were determined using a hydrogeochemistry results of  
450 As, Fe,  $F^-$  and Mn measured for rainy and winter season groundwater samples. The Visual  
451 MINTEQ 3.1 software used for determination and identification of saturation values of primary  
452 and secondary minerals. The inbuilt thermodynamic database and redox coupling species for  
453 different metals were used before each sample analysis. The obtained negative SI values  
454 signifies that these particular minerals are under unsaturated condition whereas positive SI  
455 value signifies that respective minerals are at saturation condition in study area aquifer. The  
456 reductive dissolution mechanism of iron oxy/hydroxide bearing mineral in the alluvium  
457 aquifers of Brahmaputra flood plan for high dissolved concentration of As is broadly accepted  
458 mechanism. Unsaturated condition for secondary arsenic minerals found mainly for arsenolite  
459 (Avg.  $-42 \pm 4$  &  $-49 \pm 4$ ) and claudetite (Avg.  $-42 \pm 5$  &  $-49 \pm 5$ ) in rainy and winter season  
460 groundwater samples respectively (Table 3). Therefore, these mineral results establish that the  
461 source of dissolved As in groundwater aquifer is dissolution of secondary minerals. Saturated  
462 iron-bearing minerals such as goethite (Avg.  $6 \pm 7$  &  $7 \pm 1$ ), ferrihydrite (Avg.  $4 \pm 49$  &  $5 \pm$   
463  $1$ ), and hematite (Avg.  $15 \pm 12$  &  $17 \pm 1$ ) were found in rainy and winter season groundwater  
464 samples. Saturation of these minerals in the aquifer sediment indicates that adsorption of As  
465 species on the surface of these Fe bearing mineral and primary cause for low dissolved As  
466 concentration in the As safe aquifer regions. In some regions mainly, siderite (Avg.  $-2 \pm 5$  &  $0$   
467  $\pm 1$ ) and vivianite (Avg.  $-2 \pm 17$  &  $-2 \pm 9$ ) were found in unsaturated conditions (Table 3),  
468 supports the theory of desorption mechanism from iron oxy/hydroxide minerals (Smedley and  
469 Kinniburgh 2002). These regions indicate aquifer are highly susceptible for surface water  
470 infiltration and flushing ability. The prolonged groundwater trapped in the complex aquifer  
471 strata, consequently cause for saturated Fe bearing minerals near Brahmaputra flood plain.

472 The unsaturated condition of fluorite mineral both seasons was observed as -38 to 0, have  
473 suggested that fluorite mineral is more soluble in alkaline groundwater condition than other  $F^-$   
474 bearing minerals (Apambire et al., 1997; Farooqi 2015). In acidic groundwater condition,  
475 dissolution of minerals like amphiboles, micas and apatite is more favourable than fluorite  
476 mineral (Farooqi, 2015). The groundwater aquifer were observed rich in biotite and amphibole  
477 minerals, it is an indirect indication for the high F concentration in groundwater, because  
478 fluorine substitutes a hydroxyl group from the biotite and amphiboles minerals (Edmunds and  
479 Smedley, 1996).

480 The bivariate plot results support the finding of hydrogeochemistry and Pourbaix  
481 diagram results (Figure 6). Unsaturated Fe bearing minerals were observed as hematite,  
482 goethite and ferrihydrite in rainy season (Figure 6a, 6c, 6e) whereas saturated minerals  
483 condition was observed in winter season for hematite, goethite and ferrihydrite mineral (Figure  
484 6a, 6c, 6e) which was the cause for low dissolved concentration in winter season groundwater  
485 samples. In 2D bivariate plot, unsaturated mineral condition was found even at increased  
486 dissolved concentration of As (viz. arsenolite and claudetite) and  $F^-$  (viz. fluorite) bearing  
487 minerals in both season samples (Figure 6b, 6d, 6f).

488 Table 3 shows predominant As, Fe, Mn, and  $F^-$  bearing minerals saturation index in  
489 respect of rainy and winter season groundwater samples. The presence of secondary minerals  
490 suggest that the groundwater aquifers conditions are favourable for dissolution of primary As  
491 bearing minerals and convert into secondary minerals, which was the cause for high As  
492 dissolved concentration in the study area. The selective minerals saturation indices values were  
493 found for Fe bearing minerals such as goethite, rhodochrosite, siderite, ferrihydrite, hematite,  
494 and vivianite minerals in rainy and winter season groundwater samples (Table 3). The zero  
495 saturation indices value for Fe minerals indicates that these minerals are at stable conditions.  
496 The results of low As concentration with negative saturation indices values near the foothill of

497 Meghalaya state and Brahmaputra river region indicates that dissolved concentration in  
498 groundwater aquifer is controlled by adsorption and desorption mechanism by Fe-hydroxide  
499 minerals (Smedley and Kinniburgh 2002). Similarly, unsaturated (i.e. -38) and stable (i.e.0)  
500 mineral condition for fluorite mineral suggests the primary source of  $F^-$  in groundwater aquifer.  
501 High  $F^-$  concentration in groundwater and stable mineral were observed near Meghalaya state  
502 foothill, which were further carried down by the surface water bodies (Table 3).

#### 503 **4.5 Groundwater pollution assessment**

504 The groundwater quality index analysis deciphers the applicability of groundwater in  
505 irrigation, domestic and drinking purposes. The groundwater quality index was classified into  
506 five different categories, each signifies its usage for drinking purpose and daily usage. Total  
507 48% (i.e. 45 samples) and 94% (i.e. 47 samples) of rainy and winter seasons groundwater  
508 samples respectively, were found safe for drinking water usage (Table 4). It indicates  
509 groundwater bearing aquifers are highly susceptible for surface water infiltration and dilute the  
510 dissolved As and  $F^-$  groundwater concentration.

511 Based on groundwater hydrogeochemistry results a health risk assessment analysis was  
512 carried out. The causes of primary symptoms and chronic diseases such as arsenical skin lesions  
513 and diarrhoeal disease risk were assessed by the arithmetical health risk assessment method.  
514 Results were presented in Table 5a, which depicts that children of age below 18 years old are  
515 highly susceptible (viz. 39% in rainy season and 64% in winter season) for As ingestion  
516 diseases. In Table 5b, suggests that people of age above 18 years old (i.e. female and male)  
517 were found highly susceptible to hyper pigmentation and keratosis. In a total highest affected  
518 population was female, in the rainy season total of 7112 (i.e. 33%) and winter season 5952 (i.e.  
519 52%) female population were found susceptible to dermal effect (Table 5b). The overall results  
520 of health risk assessment suggest that in a total 29,616 population of Guwahati city is at a risk

521 of As contaminated groundwater pollution. The fluorosis effect on the present population was  
522 not found at significant risk in this health risk assessment method.

#### 523 **4.6 3D spatial and depth wise concentration distribution**

524 Ordinary kriging method with combination of different variogram models was used to  
525 understand the concentration gradient of Fe, As, Mn, and F<sup>-</sup> in different depth aquifers of the  
526 study area (Figure 7, 8, 9 & 10). The study area was divided into three-dimensional grid cells,  
527 it is horizontally divided into 150 × 150 cells and vertically it is divided into 15 cells because  
528 predominantly 15 layers were found in lithological data provided by PHED Assam. Different  
529 variogram models such as gaussian, exponential and spherical were used to understand reliable  
530 method results which could help to identify the safe groundwater regions in the study area.  
531 High As and F<sup>-</sup> contaminated regions were found along the boundary of the Khasi foothill of  
532 the Meghalaya state on the south-east side of Guwahati city. Gaussian model function results  
533 were found well corroborated with the measured dissolved concentration of groundwater  
534 samples for Fe, As, Mn, and F<sup>-</sup> in the study area. The contaminants in all aquifers were not  
535 found varying in concentration, which suggests that partially homogeneous aquifer materials  
536 are present in the study area (Figure 7, 8, 9 & 10). Dissolved Fe distribution in the aquifer was  
537 depicting similar trends of As high and low concentrations which was measured in analytical  
538 method, it indicates that Fe-oxy/hydroxide adsorption and desorption mechanism control the  
539 As concentration in different depth of study area aquifers.

540 Influence of tributary river (i.e. Bharalu river) and Brahmaputra river water infiltration  
541 was observed in both seasons aquifers depths (Figure 7a,b & 9a,b). Comparatively opposite  
542 trends were observed between Mn and Fe concentration gradient in all aquifer depths for rainy  
543 groundwater samples (Figure 7c,d, 8c,d, 9c,d & 10c,d). Distribution of F<sup>-</sup> in the Gaussian  
544 model kriging indicated that the eastern region of Guwahati city is a predominantly geogenic  
545 source for the study area (Figure 6c,d, 7c,d, 8c,d and 9c,d). Concentration distribution within

546 all aquifers was observed to be similar, which suggested that vertical distribution of Fe, As, Mn  
547 and F<sup>-</sup> are controlled by artificial activities such as groundwater pumped out for industrial,  
548 drinking and domestic purposes. Such concentration distribution variability was observed in  
549 contaminant transport modelling in West Bengal (Mukherjee et al., 2007) and Assam state of  
550 India (Sathe and Mahanta 2019a).

## 551 5 Conclusion

552 In study area, due to rapid development and increase in population, people are facing  
553 shortage for safe drinking water, since last decade. The residential and commercial industries  
554 are using groundwater source for daily usage. The results of hydrogeochemistry, statistical  
555 analysis and minerals saturation indices for the analysed groundwater samples have deciphered  
556 that the geogenic sources of As and F<sup>-</sup> bearing minerals are present in the groundwater aquifers  
557 of the study area. Prevalent mechanisms identified such as ion exchange, weathering (viz. that  
558 of carbonate, silicate minerals), evaporation, precipitation (such as mineralization of siderite,  
559 hematite, goethite, and ferrihydrite) and reductive dissolution of different minerals (viz. Fe-  
560 oxy/hydroxide, fluorite, arsenolite, claudetite) in alluvial aquifers. The measured ORP values  
561 during groundwater sampling with elevated Fe and As concentration groundwater samples  
562 support the reductive dissolution mechanism of iron oxy/hydroxide minerals was the primary  
563 cause for high As concentration in the groundwater samples.

564 The overall hydrogeochemistry of rainy and winter season data concludes that the shallow  
565 depth aquifers are influenced by surface water infiltration. The identified hydrogeochemical  
566 facies such as Na<sup>+</sup>-Cl<sup>-</sup> and SO<sub>4</sub><sup>-2</sup>-Ca<sup>+2</sup> suggest that the groundwater has long residential time,  
567 which allows to the Fe, As, F<sup>-</sup> and Ca<sup>+2</sup> bearing minerals to precipitate and interact in the  
568 aquifer. Gibbs diagram revealed that the groundwater of the alluvium aquifer is susceptible to  
569 dissolution mechanism of rock-water interaction and precipitation of minerals. The high



570 concentrations of  $\text{Na}^+$ ,  $\text{Ca}^{+2}$  and  $\text{HCO}_3^-$  support ion exchange process to be prevailing in the  
571 groundwater aquifer. Results of this study agree with the mineralization and dissolution  
572 mechanism observed in minerals saturation indices found for dominant *As*,  $\text{F}^-$ , *Fe* and *Mn*  
573 bearing minerals. The groundwater quality index results identified that majority of winter  
574 season groundwater samples fall in excellent to good water category, which suggest that winter  
575 groundwater is likely to be more suitable than rainy groundwater samples for drinking water  
576 purposes, whereas 52% of rainy season groundwater samples were classified as unsuitable for  
577 drinking water purposes. The main cause behind is depletion of groundwater table and  
578 simultaneously, evaporation and adsorption of dissolved *As* and  $\text{F}^-$  on soil matrix. Whereas, in  
579 rainy season groundwater table rises up and inducing reducing condition at shallow depth  
580 aquifer, which increases dissolved concentration of *As* and  $\text{F}^-$  in groundwater.

581         Arithmetical health risk assessment from rainy and winter season groundwater samples  
582 has predicted that children population of around 39 % and 64 % may suffer by *As* ingestion  
583 risk. Furthermore, rainy and winter season groundwater samples have revealed that 4% and 2%  
584 respectively, children population may suffer by an arsenical skin lesion (i.e. dermal effect). The  
585 health risk assessment results have suggested that considerably high percentage of dermal  
586 effect may be found in the women population than the male population in the study area.

587         Ordinary kriging method results for different depths aquifers have suggested that the  
588 closely spaced contours indicates groundwater extraction rate is high from these regions. From  
589 this study it can be concluded that the aquifer of depth 250 ft. to 500 ft. can be delineated as  
590 safe aquifer and can be used for installation of deep tube wells for drinking water purposes.  
591 Ground water quality monitoring result for this study area from year 2019 to 2020, will help  
592 the public authorities to provide a pertinent and technologically viable solution to the study  
593 area peoples.

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