Assessment of Water Quality for the Groundwater Resources of Urbanized Part of the Nagpur District, Maharashtra (India)

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Abstract   Hydrogeochemical characterization of groundwater samples representing the urbanized and industrialised parts of Nagpur district, situated in Central India has been carried out in the pre-monsoon season of 2011. The groundwater quality assessment study is attempted by examining the physicochemical parameters *viz*. pH, EC, TDS, Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3, Cl^- and SO_4^{2-}. On the basis of ionic concentrations, the groundwater quality is evaluated in favour of its utility for drinking and irrigation purposes. The abundance of cations and anions in the analysed groundwater samples is, Ca^{2+} (%) > Mg^{2+} (%) > Na^+ (%) > K^+ (%), and HCO_3^- (%) > Cl^- (%) > SO_4^{2-} (%) > NO_3^- (%) > F^- (%), respectively. The Piper trilinear diagram reflects almost Ca^{2+}- HCO_3^- type hydrochemical facies (alkaline earth exceeds alkalis and weak acids exceed strong acids). Due to higher concentration of total dissolved solids, total hardness and magnesium, majority of the samples belongs to the very hard type. Schoeller index values corroborate existence of Base Exchange reaction. As per the United States Salinity (USSL) diagram the groundwater samples in the study area are free from sodium hazards; however, their salinity hazard shows low to very high range. Majority of the groundwater samples fall in rock dominant region and confirms existence of rock-water interaction on the Gibbs plot. A comparative study of groundwater samples on the basis of drinking water standards shows that many of the groundwater samples are unsuitable for drinking. The corrosivity ratio illustrated that four groundwater samples show higher corrosivity ratio, leads to loss in hydraulic capacity of pipes. It is inferred that the study area is moderately suitable for agricultural activities. The analytical results reveals that deep aquifer in the study area is less polluted as compared to the shallow one. The impact of anthropogenic activities on the groundwater quality is also investigated and accordingly the appropriate management measures are recommended.

Keywords: *hydrogeochemistry, anthropogenic input, urbanized and industrialised parts, nagpur district, India*

1. Introduction

India, the second largest populous nation in the world, is witnessing economic development in the present era. The developmental scenario which is associated with rapid growth in population and urbanization has resulted into tremendous increase of groundwater demand [1,2]. Such activities can exert significant pressure on hydrogeological system on a sequential and spatial scale, mainly by introducing contaminants into the underlying aquifers. As a result, surface and groundwater quality degradation is the burning issue echoing on the horizon of environment research in this country [3,4,5,6].

Apart from the surface water, shallow aquifers water is most likely to be used for the basic needs of human beings. Such groundwater sources, hoisted in the shallow aquifers are more susceptible to surface contamination and have significant potential for being contaminated by the pollutants from domestic as well as agricultural and industrial sources. Pollution from the water table aquifers habitually move towards deeper aquifers, if they are not confined from pollution or when they are intensively developed. Groundwater resources, therefore, are becoming extremely vulnerable to a multitude of anthropogenic pollution sources [7]. In addition to this, the dissolved ions in groundwater are continuously added due to weathering of minerals [8,9]. The nature of the rock formations, topography, soils, atmospheric precipitation, quality of the

recharged water and subsurface geochemical process are some of the parameters that affect groundwater quality [10,11]. Hence, for knowing usefulness of water as a neutral agent in the various purposes to understanding its physical and chemical properties is inevitable

The degree of human dependency on water and scarcity of usable water (0.002% of total water) renders its conservation on priority basis [12]. Hydrochemical evaluation of groundwater system is thus usually based on the availability of large amount of information concerning groundwater chemistry [13]. Geochemical processes, taking place within groundwater and their reactions with the aquifer materials, are responsible for changes in groundwater chemistry [14,15]. The assessment and classification of groundwater based on its quality can be obtained by analyzing its chemical characteristics. Variations in ion chemistry of groundwater are used to identify geochemical processes that control the groundwater quality. Ion exchange reaction is the process of replacement of ions absorbed from the surrounding aquifers by ions in the solution.

This study predicts the overall groundwater quality and hydrogeochemical characteristics of the study area which was not focused in the earlier studies. In the present area, groundwater is the main source of dependency. The aim of the study is therefore highlighted to assess the geochemical processes controlling the water composition and also intends to identify the hydrochemical and anthropogenic contamination factors responsible for deterioration of water quality using different physico-chemical parameters. Being situated on the periphery of the industrialized and urban parts, the impact of the involved processes is expected on the groundwater regime of the study area.

2. Study Area

Nagpur, one of the fastest growing industrialized cities in Central India, is the third largest city in Maharashtra state [16,17]. This region is situated practically at the geographical centre of India and lies in between latitude 21°06′ - 21°12'N and longitudes 79°0′ - 79°10'E with 312 m above mean sea level. The study area constitutes the South-Western parts of the Nagpur Urban and is covered between the longitudes 78°55′47″E - 79°2′47″ E and latitudes 21°01′30″N - 21°09′19″ N, covering toposheet numbers 55 O/4 and K/16 of the Survey of India (Figure 1). This area is vulnerable to groundwater pollution due to the combined effect of industrialization and anthropogenic activities.

2.1. Geological Setup and Hydrogeology

Geologically, the area is occupied by flat topped and terraced featured basaltic lava flows. Most of the area is plain and covered by black cotton soil (Figure 2). Mainly, two types of hydrogeological units of basaltic lava flow have been identified in the study area i.e. vesicular unit (confined to upper part of the flow) and massive unit (confined to lower part of the flow). Deccan Trap basaltic lava flows are underlain by the older formations, *viz.* granitic gneisses, quartzites and muscovite/biotite schist, etc. of the Archean age [18].
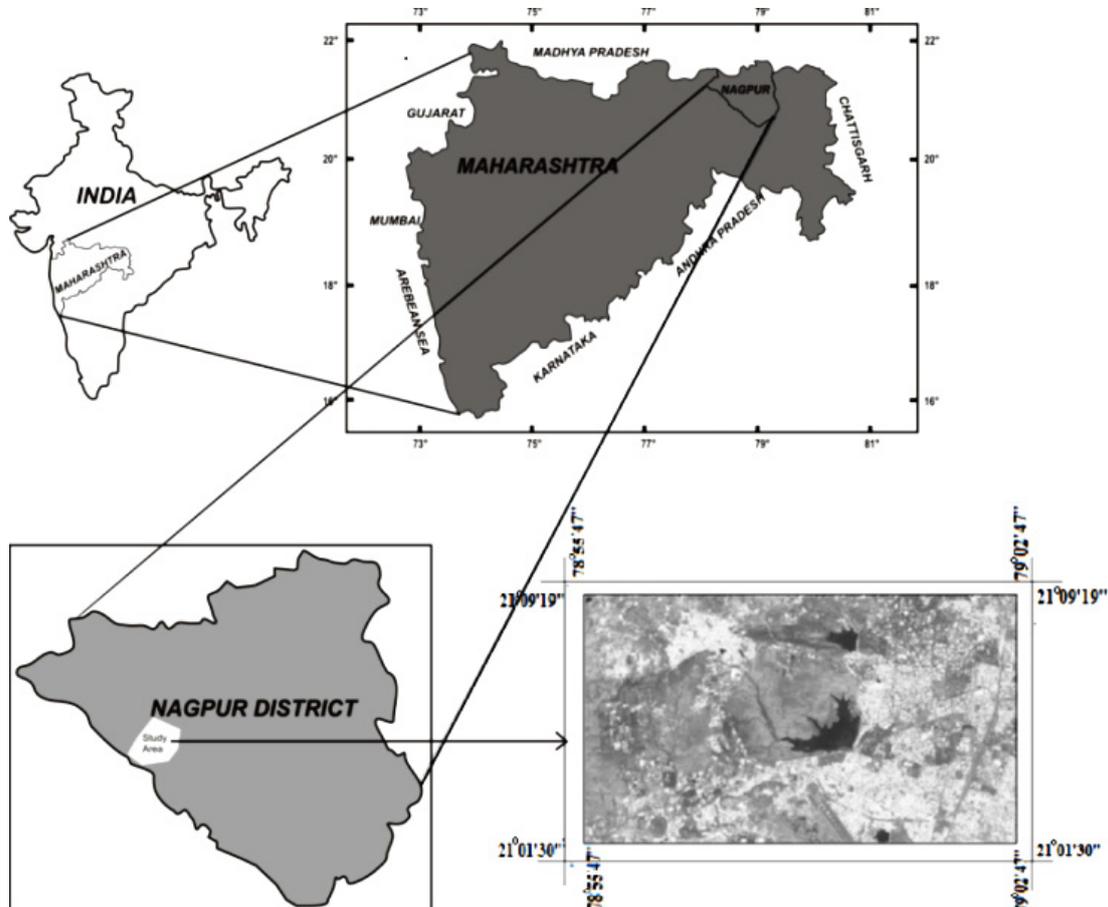

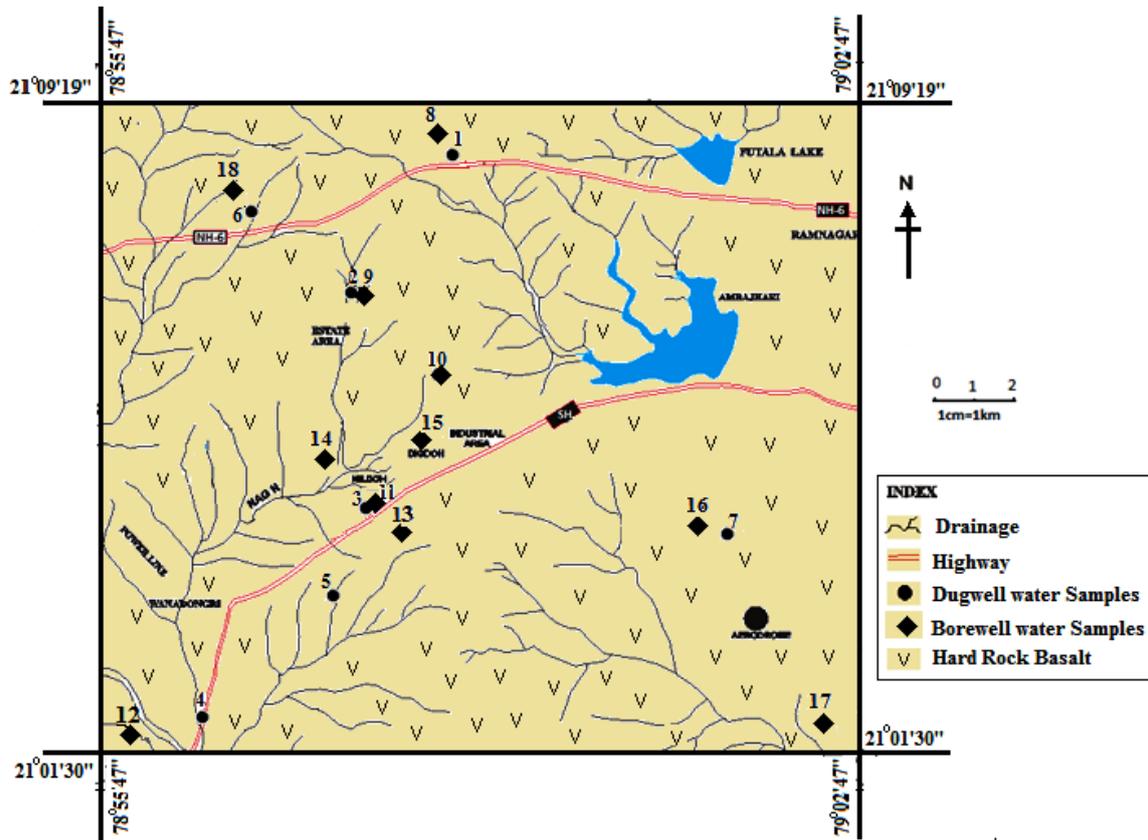**Figure 1.** Index map of the study area

Figure 2. Sampling location map of the study area

The availability of groundwater in the Nagpur district is mainly controlled by rocks of Archeans, Gondwana, Lameta, Deccan traps and Alluvium. In the Deccan trap areas, water bearing formation depends on the degree and the depth of weathering, which varies between 15 and 25 m from place to place, depending upon the nature of topography. The permeability of the weathered zone is low to medium and accordingly the yields of dugwell also vary. The high yields are generally associated with the presence of fractures [18,19]. Hydrogeology plays an important role in both the dispersion as well as prevention of the pollutant into the groundwater system. In this case, the shallow aquifer is representing weathered / jointed basalt; whereas, deeper aquifer in the area is representing jointed/ fractured basalt.

In the present work, a selection standard was established to identify suitable sampling sites for the groundwater quality assessment and background survey has also been carried out before the sampling. Samples are collected only from those dugwells and borewells which are in use either for domestic or irrigation purposes. In order to understand the chemical composition of groundwater and variation in its hydrochemical fabric, total eighteen (18) groundwater samples were collected from various borewells and dugwells in the study area (Figure 2; Table 1) during the pre-monsoon season of year 2011. The chemical reagents, including indicators and buffers, were of analytical grade and the standardization of reagents and solutions was in accordance with standard methods of water chemical analysis [20].

The physical parameters like pH, temperature and electrical conductivity (EC) were measured in the field itself with the help of portable water analysis kit.

Subsequently, the parameters like calcium, magnesium, carbonate, bicarbonate were analysed by volumetric (titration) method by following the APHA [21] and NEERI [22] standards. Whereas, for the determination of fluorine, nitrate and sulphate, the systronic make spectrophotometer (UV-VIS model) was employed. However, for the determination of sodium and potassium content, the flame photometer (ELICO) instrument was used. The hydro-chemical composition of total 18 groundwater samples of study area is given in Table 1.

3. Results and Discussion

3.1. Groundwater Quality with its Hydrochemical Characteristics

The hydrochemical investigation of groundwater provides information about the source and extent of groundwater pollution and determines its utility for various purposes. Depending upon some specific standards the groundwater quality can be determined for its suitability for different purposes. In present study the standards of World Health Organization [24] is utilised to decide the potability of groundwater for drinking purpose. Different parameter indices for rating the water quality of study area are given in Table 1.

The pH value varies from 6.9-7.5 in dugwell, 6.5-7.2 in borewell water samples indicating slight acidic to alkaline nature. The aquifer in the study area is mostly vesicular basalt which imparts alkaline nature of water. The safe limit of pH lies between 6.5 and 8.5. The slight acidic nature of a few samples indicates impact of industrial

influence on the groundwater quality. The value of conductivity in study area ranges between 755-1720 µS/cm with an average 1239 µS/cm and 719-5010 µS/cm with an average 1496 µS/cm in dugwell and borewell water, respectively. For drinking water the recommended value for EC is 1400 µS/cm. The samples exceeding the safe limit values may reflect the dissolution of minerals, anthropogenic activities and geochemical processes prevailing in the region [25].

TDS indicates salinity of water. In the study area, the total dissolved solid concentration varies from 522-1141 mg/L with an average 813 mg/L and 511-2564 mg/L with an average 934 mg/L in dugwell and borewell water,

respectively. The permissible limit for TDS as suggested by the WHO [24] is 1000 mg/L. The TDS results reveal that most of water samples are within permissible limit except two (dugwell -5 and borewell -16). Intrusion of waste water from the surrounding industrial and agricultural lands may be the reason for increase in the TDS in the study area. The distribution of the TDS for shallow and deeper aquifers is presented in Fig. 3 and Fig. 4. Both the figures indicate that, in major part of the area, the TDS of ground water is within permissible limit of the WHO, except in Southern part in case of shallow aquifer and in Central part in case of deeper aquifer where TDS is above permissible limit.
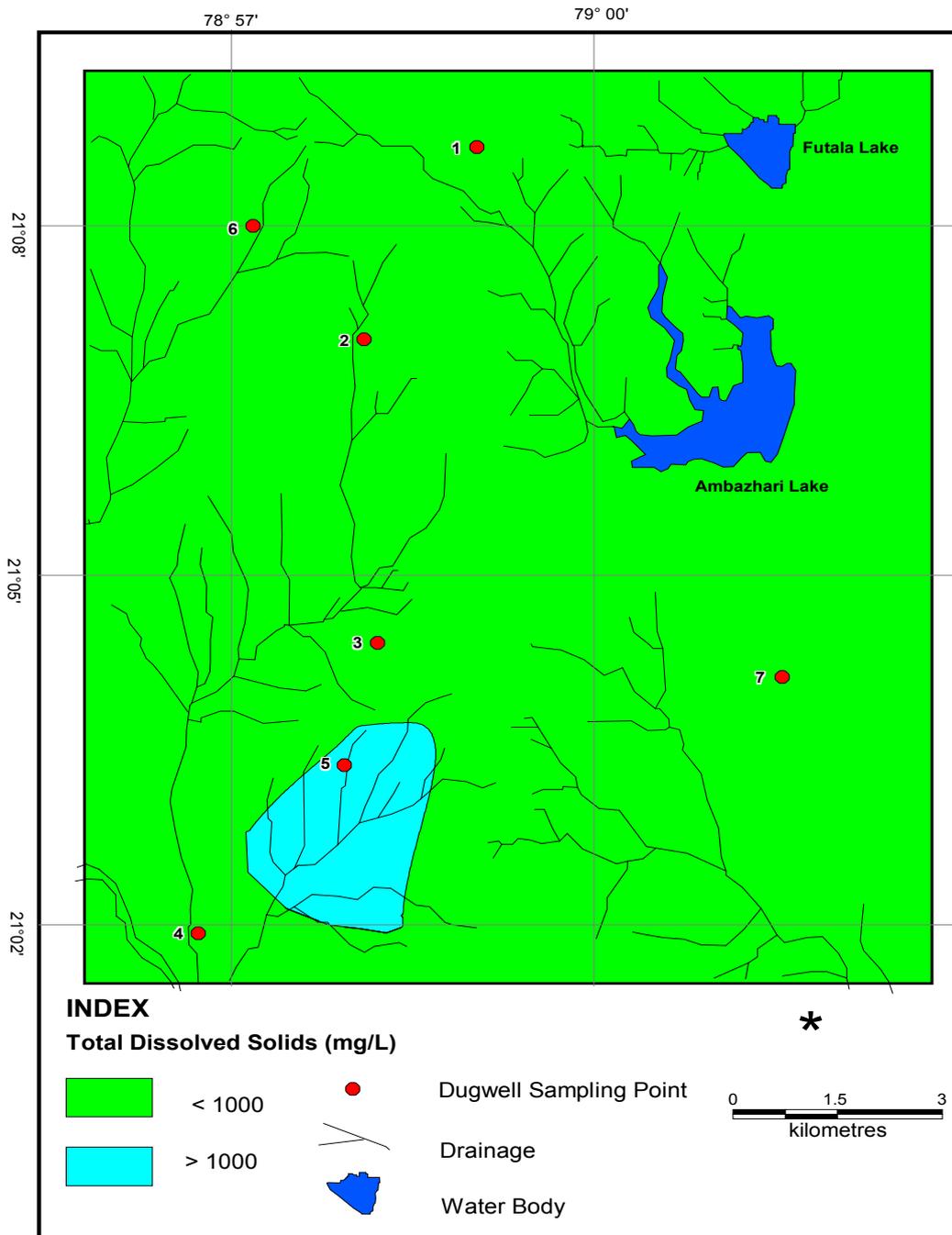

Figure 3. Distribution of TDS in shallow and deeper aquifers

DISTRIBUTION OF TOTAL DISSOLVED SOLIDS IN DEEPER AQUIFER
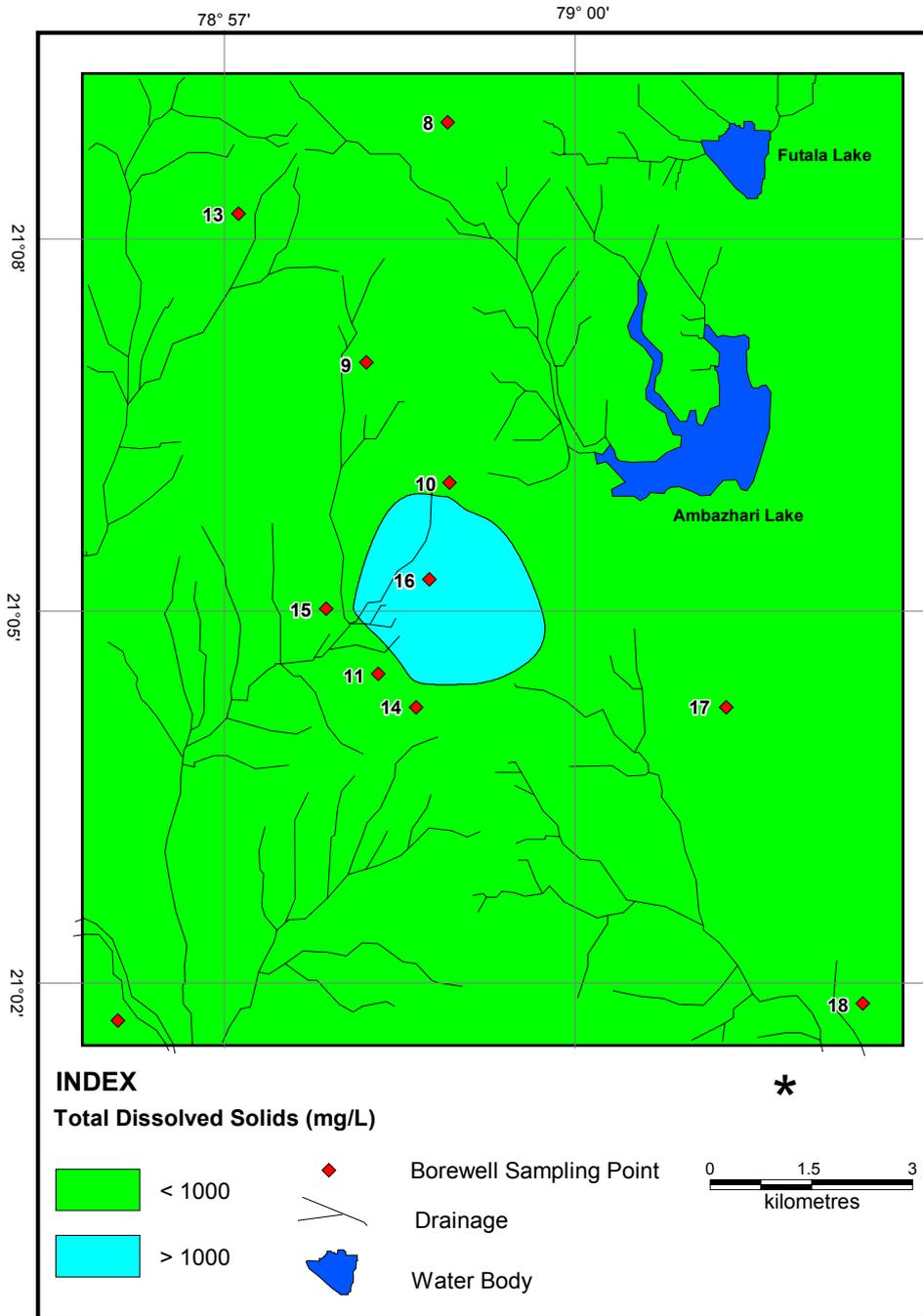### URBANISED PART OF NAGPUR DISTRICT, MAHARASHTRA

Figure 4. Distribution of TDS in shallow and deeper aquifers

Classification of groundwater by Devis and De Wiest [26] based on TDS shows up to 500 mg/L (desirable for drinking); 500–1,000 mg/L (permissible for drinking) and up to 3,000 mg/L (useful for agricultural purposes). Based on this classification, it is observed that all the samples are permissible for drinking, except two which are not suitable for drinking but can be used for agricultural purposes.

Hardness is the property of water which prevents lather (foam) formation with soap and increases the boiling point of water. According to the WHO [24], total hardness should not exceed 500 mg/L for drinking purpose. The hardness of water during pre-monsoon season ranges from 325-835 mg/L (with an average of 561mg/L) and 363-2102 mg/L (with an average of 667mg/L) for dugwell and borewell water, respectively. In shallow aquifer, the hardness is within permissible limits in entire Northern and Southern part of the area (Figure 5); whereas, hardness above permissible limits is observed in Eastern and Central parts. Many of the samples of deeper aquifer except few exceed the WHO limit for drinking purposes as evident from the Figure 6, wherein major area is above permissible limit and small Eastern area is having hardness below the permissible limit of the WHO. Beyond this limit it leads to encrustation in water supply structure and adverse effects on domestic use.

DISTRIBUTION OF TOTAL HARDNESS IN SHALLOW AQUIFER
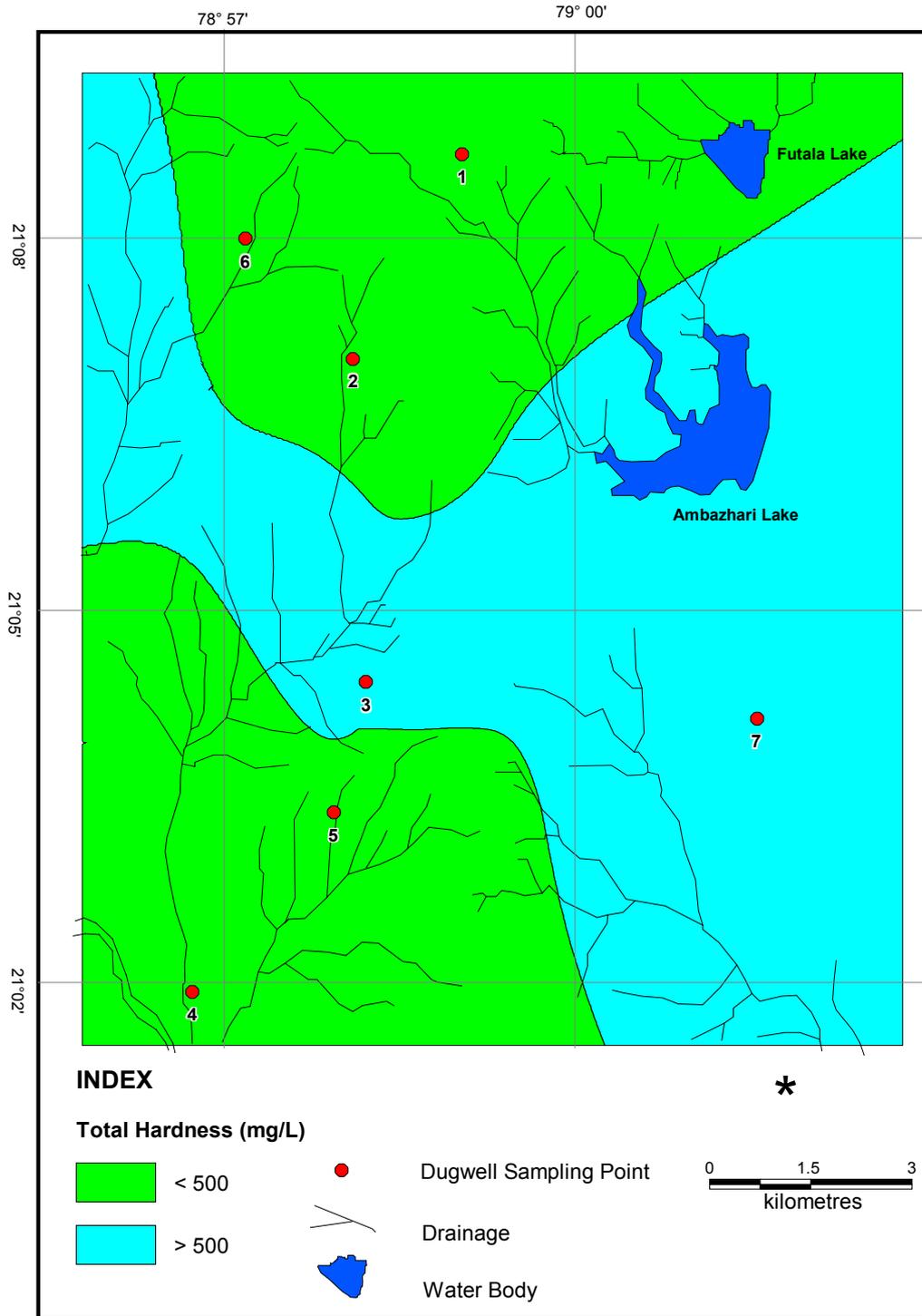### URBANISED PART OF NAGPUR DISTRICT, MAHARASHTRA

Figure 5. Distribution of Total Hardness in shallow and deeper aquifers

Classification suggested by Sawyer and McCarty [27] for the groundwater containing total hardness between 0 and 75 mg/L is soft, 75-150 mg/L is moderately hard, and 150-300 mg/L is hard and above 300 mg/L is very hard water. It is observed that, all the samples fall under the 'very hard' type of water category.

The abundance of cations in water is $Ca^{2+} > Mg^{2+} > Na^+ > K^+$. In few groundwater samples represent the cation Mg^{2+} dominates Ca^+. Even though, there is no change in the order of abundance. Calcium comes in water mainly from the rocks by leaching. The desirable limit of Ca is 75 mg/L for drinking purpose, beyond this limit it leads to encrustation in water supply structure and adverse effects on domestic use. It may be extended up to 200 mg/L [24]. The calcium in study area, during pre-monsoon season ranges from 40-165 mg/L (with an average 107 mg/L) in dugwells and 30- 513 mg/L (with an average 136 mg/L) in borewells. All the water samples (except one, borewell -16) fall under the permissible limit.

DISTRIBUTION OF TOTAL HARDNESS IN DEEPER AQUIFER
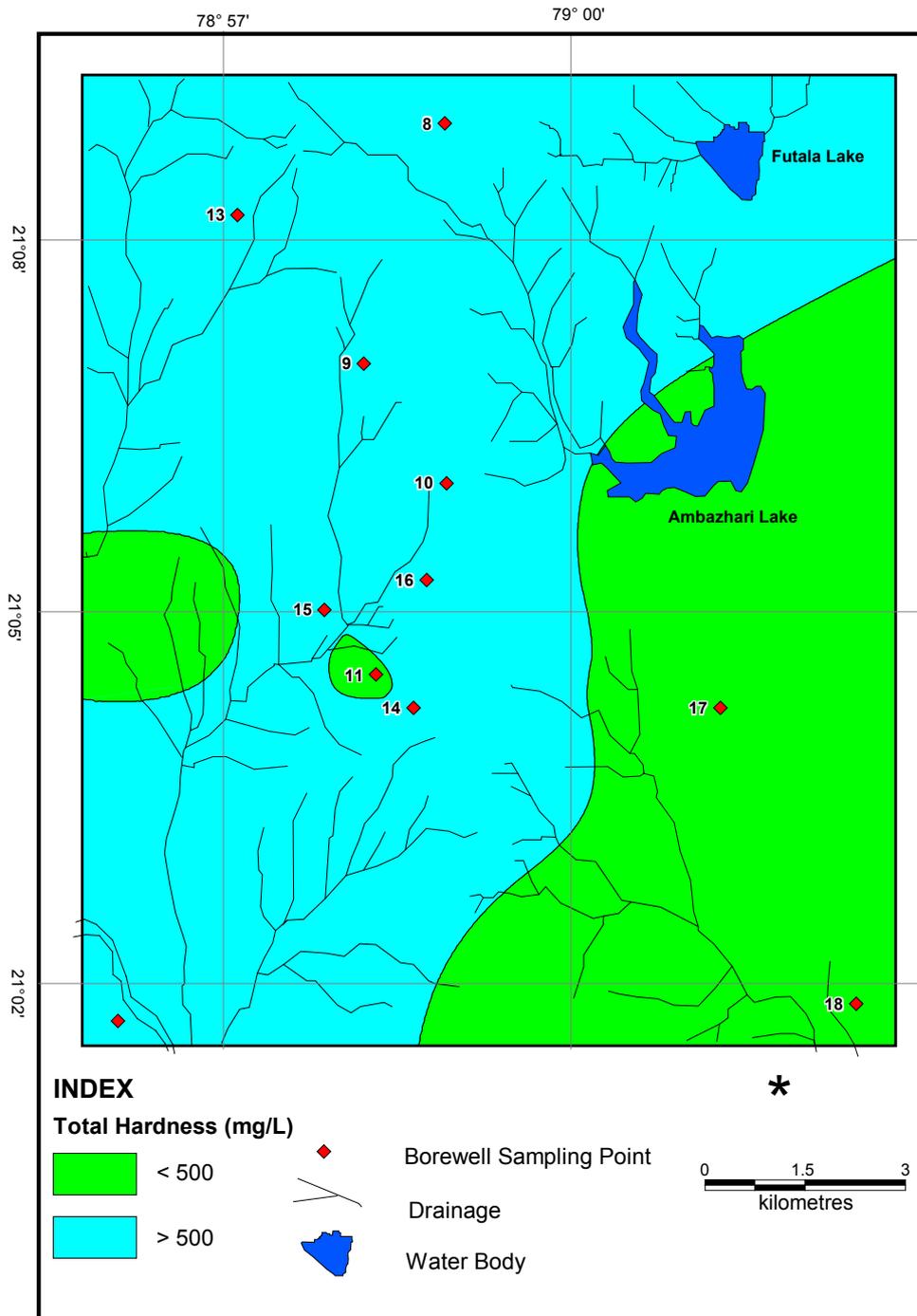### URBANISED PART OF NAGPUR DISTRICT, MAHARASHTRA

Figure 6. Distribution of Total Hardness in shallow and deeper aquifers

Magnesium occurs in all kinds of natural waters with calcium, but its concentration remains generally lower than that of calcium. Concentration of magnesium in the study area ranges from 45- 133 mg/L (with an average value of 72 mg/L) and 44-200 mg/L (with an average value of 80 mg/L) for dugwells and borewells respectively. The WHO permissible limit for Mg is 50 mg/L. All the samples from both dugwell and borewell exceed the permissible limit except two (one each from dugwell - 3 and borewell - 8). The spatial distribution of magnesium in groundwater of shallow and deeper aquifers shows that

in major part, the magnesium is above permissible limits of the WHO rendering its unsuitability for drinking purpose except in Central part in shallow aquifer (Figure 7) and North Eastern parts in deeper aquifer (Figure 8).

Sodium salts are readily soluble in water and remain in solution unless extracted during evaporation. Sodium is an important element in determining suitability of groundwater for irrigation purpose. Sodium content in the samples falls between a range of 18-34 mg/L (with an average 27 mg/L) and 13-170 mg/L (with an average 37 mg/L), for dugwell and borewell, respectively. Sodium content in drinking

water can be allowed up to 200 mg/L [24]. Sodium contents are within safe limit for all the groundwater samples for dugwells as well as borewells in the study area. The potassium content shows a narrow range from 2 to 9.70 mg/L (with an average 5 mg/L) and 1.50 to 3.10 mg/L (with an average 2.2 mg/L) for dugwell and borewell, respectively. These values indicate that all the groundwater samples fall under safe limit [24].

The major anion abundance is in the order $HCO_3^- > Cl^- > SO_4^{2-} > F^- > NO_3^-$. The bicarbonate ion concentration ranges from 270-478 mg/L (with an average 374 mg/L) and 322-918 mg/L (with an average 434 mg/L) for dugwells and borewells, respectively. The bicarbonates in groundwater may be due to the oxidation and decomposition of organic pollutants [28] and because that CO_2 reacts with soil and releases HCO_3^- into the groundwater [29]. A wide range in chloride content has been observed i.e., 71-282 mg/L (with an average 174 mg/L) and 62-332 mg/L (with an average 168 mg/L) for dugwells and borewells respectively. The permissible limit for chloride is 250 mg/L [24]. All the groundwater samples fall within the safe potable limit except a few as evident from the spatial distribution of Chloride, wherein, small area in Southwest corner is occupied by samples of higher chloride concentration in shallow aquifer (Figure 9) and only one sample in Central part is having concentration beyond the WHO limit, rendering it unsuitable for drinking in case of deeper aquifer (Figure 10).
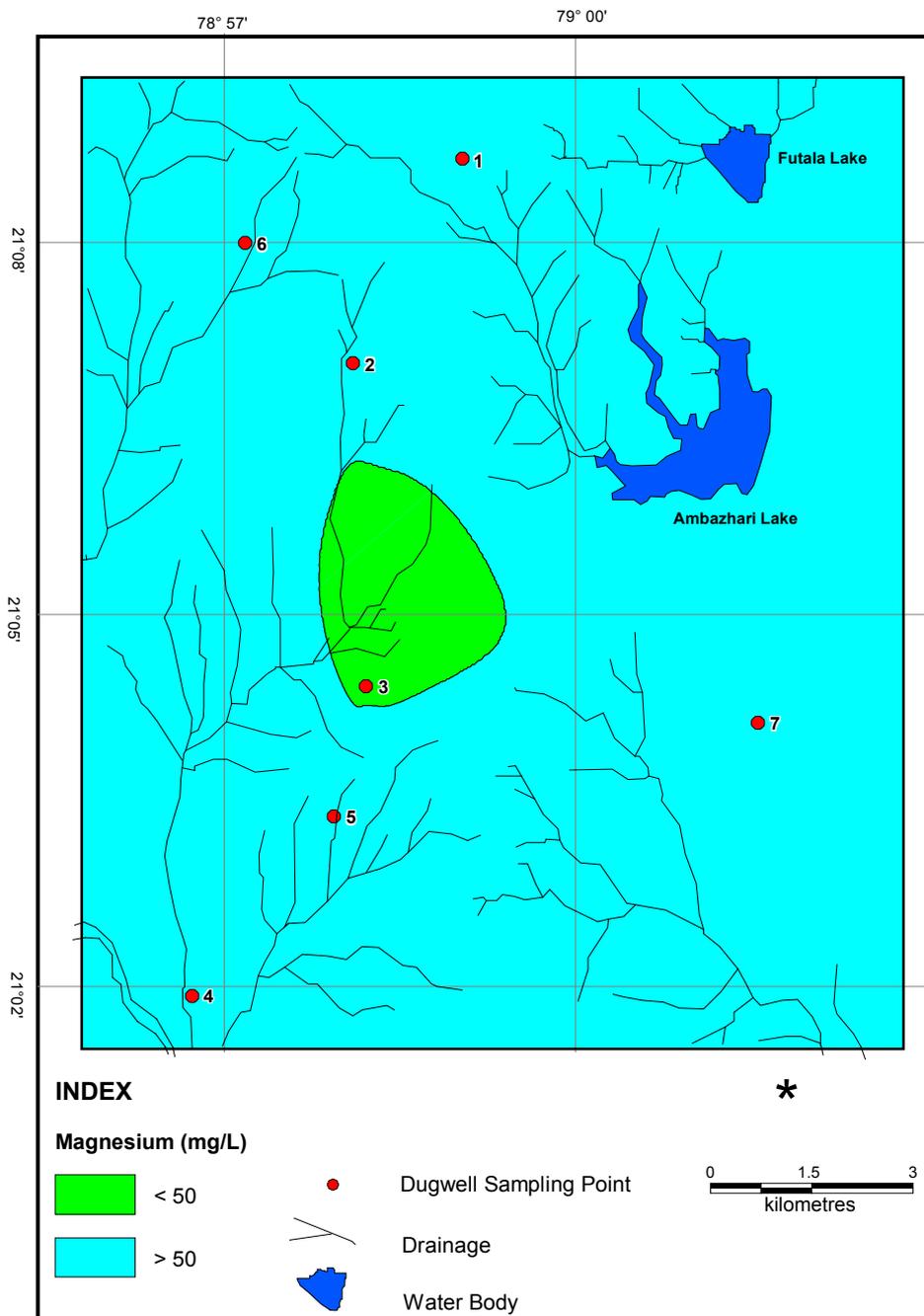

Figure 7. Distribution of Magnesium in shallow and deeper aquifers

DISTRIBUTION OF MAGNESIUM IN DEEPER AQUIFER
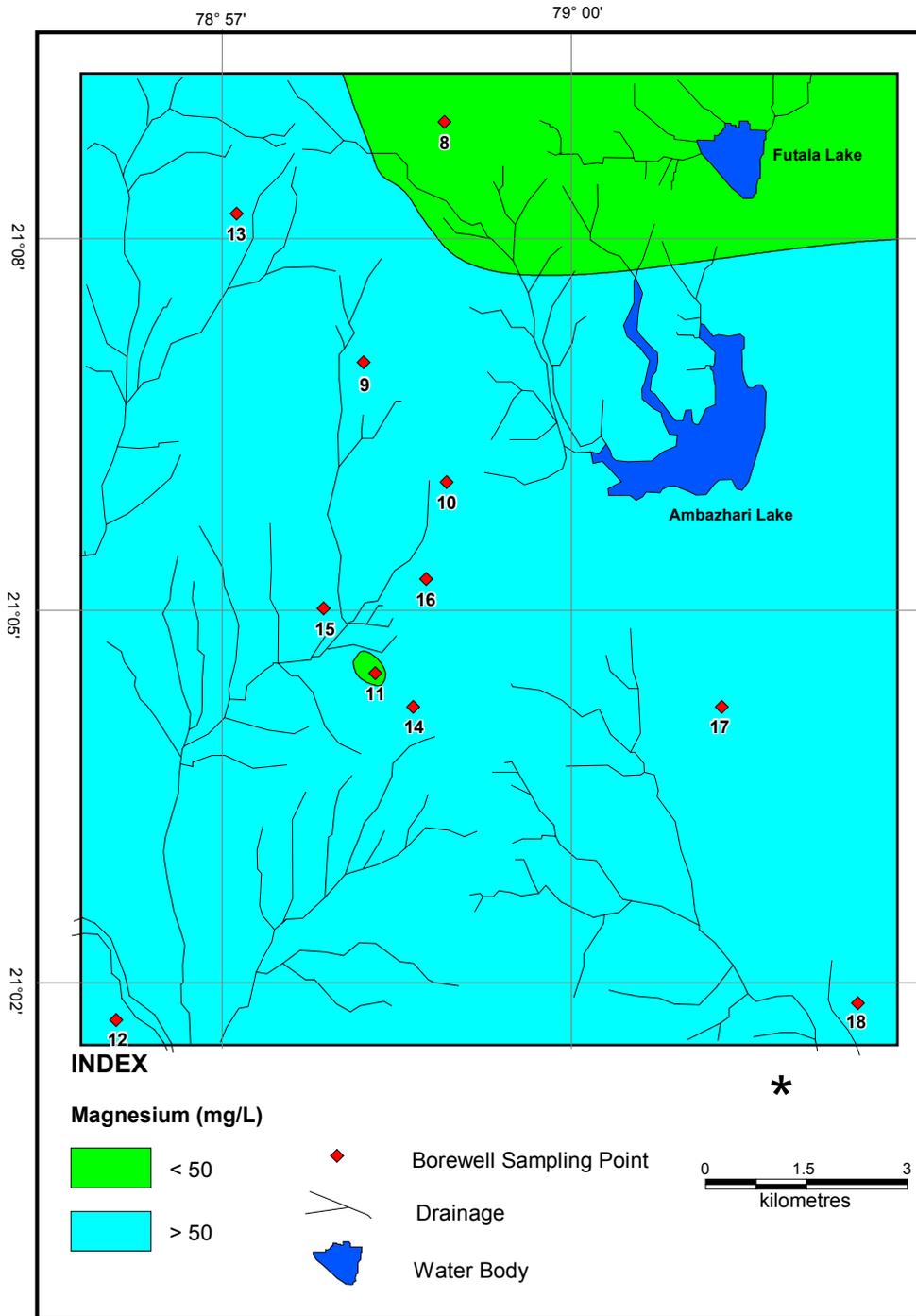## URBANISED PART OF NAGPUR DISTRICT, MAHARASHTRA

Figure 8. Distribution of Magnesium in shallow and deeper aquifers

The chlorine in the groundwater originates from both the natural and anthropogenic sources like runoff containing inorganic fertilisers, animal feeds, irrigation drainage and industrial effluents.

Sulphate is naturally occurring anion in all kinds of natural waters. The sulphate content in these samples depict a wide range from 3-96 mg/L (with an average 53 mg/L) and 0.0- 427.4 mg/L (with an average 76 mg/L) for dugwells and borewells, respectively. A limit of sulphate 250 mg/L has been suggested for drinking purposes [24]. This clearly shows that all the samples (except one borewell sample-16) come under the desirable limit of sulphate.

The fluoride in groundwater is mainly due to leaching of fluoride bearing minerals during rock-water interaction. Anthropogenic sources may cause fluoride pollution in groundwater. The fluoride content is varying between 0.24-0.93 mg/L (with an average 0.57 mg/L) and 0.25-0.82 mg/L (with an average 0.6 mg/L) for dugwell and borewell water respectively. The potable limit of fluoride is 1.5 mg/L [24]. It clearly shows that all the samples of the study area are falling within safe limit for fluoride

content. Nitrates are widely present in substantial quantities in soil, in most waters, and in plants including vegetables (WHO 1978). Limit of general acceptability of nitrate for drinking water is 50 mg/L [24]. Whereas, nitrate content show variation between 1.5 - 3.8 mg/ L (with an average 2.4 mg/L) and 0.12-3.11 mg/L (with an average 1.27 mg/L) for dugwells and borewells, respectively. This shows that all the samples come under the desirable limit of nitrate.

The TDS is above permissible limit in Southern part in case of shallow aquifer and in Central part in case of deeper aquifer. The Total hardness is above permissible limits in Eastern and Central parts in case of shallow aquifer and in Northern, Western and Southern areas in case of deeper aquifer. The Magnesium is above permissible limits illustrating its unsuitability for drinking purpose in entire study area except Central part in shallow aquifer and North Eastern parts in deeper aquifer. In case of Chloride, the higher values are observed in South-west corner in shallow aquifer and in Central part in deeper aquifer. Thus, the spatial distribution of these four parameters indicate that the areas of contamination in shallow and deeper aquifers do not overlap and are occupying different areas, so, lateral and vertical extent of the contamination has been deciphered in the study area.
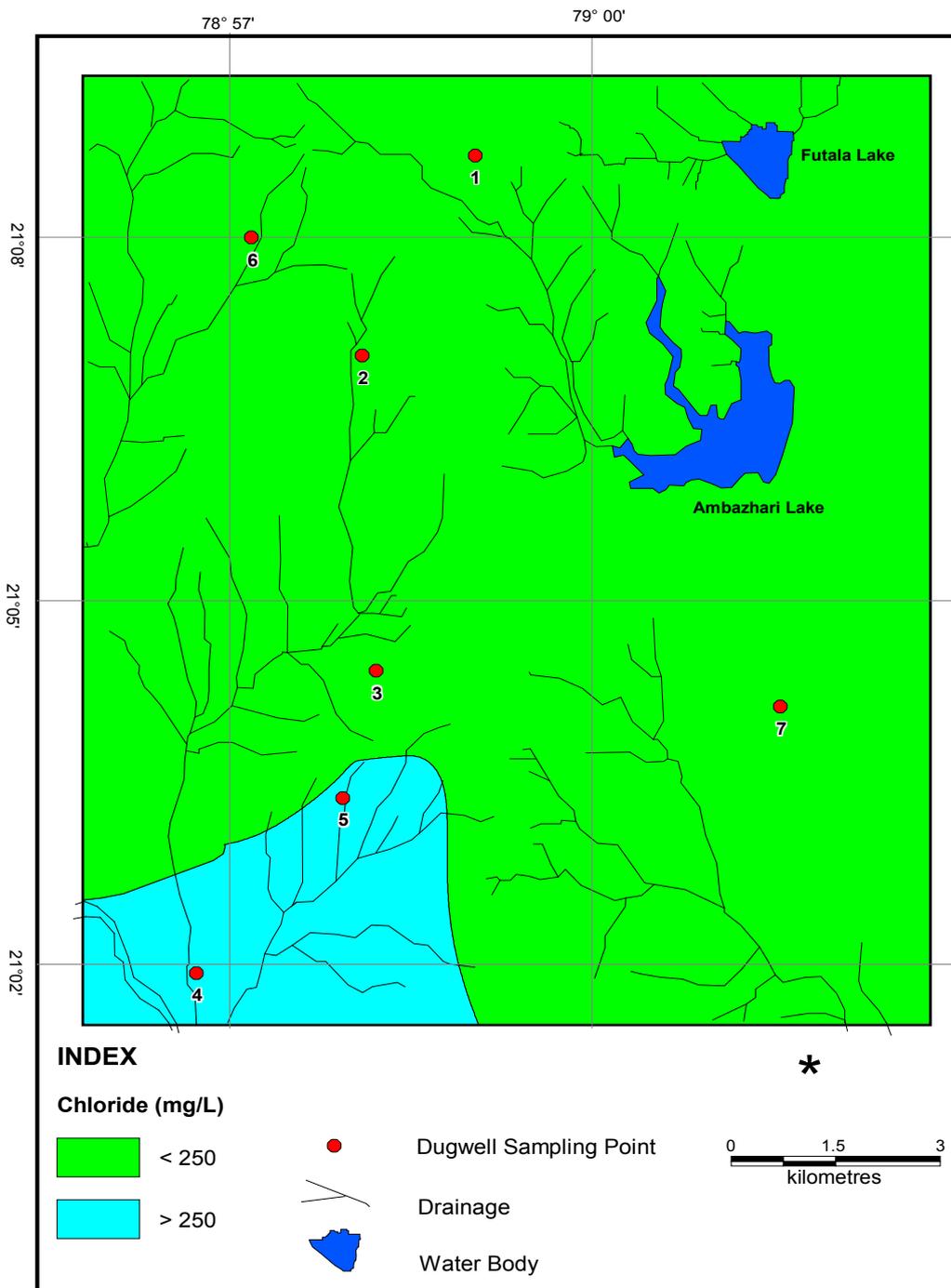

Figure 9. Distribution of Chloride in shallow and deeper aquifers

DISTRIBUTION OF CHLORIDE IN DEEPER AQUIFER
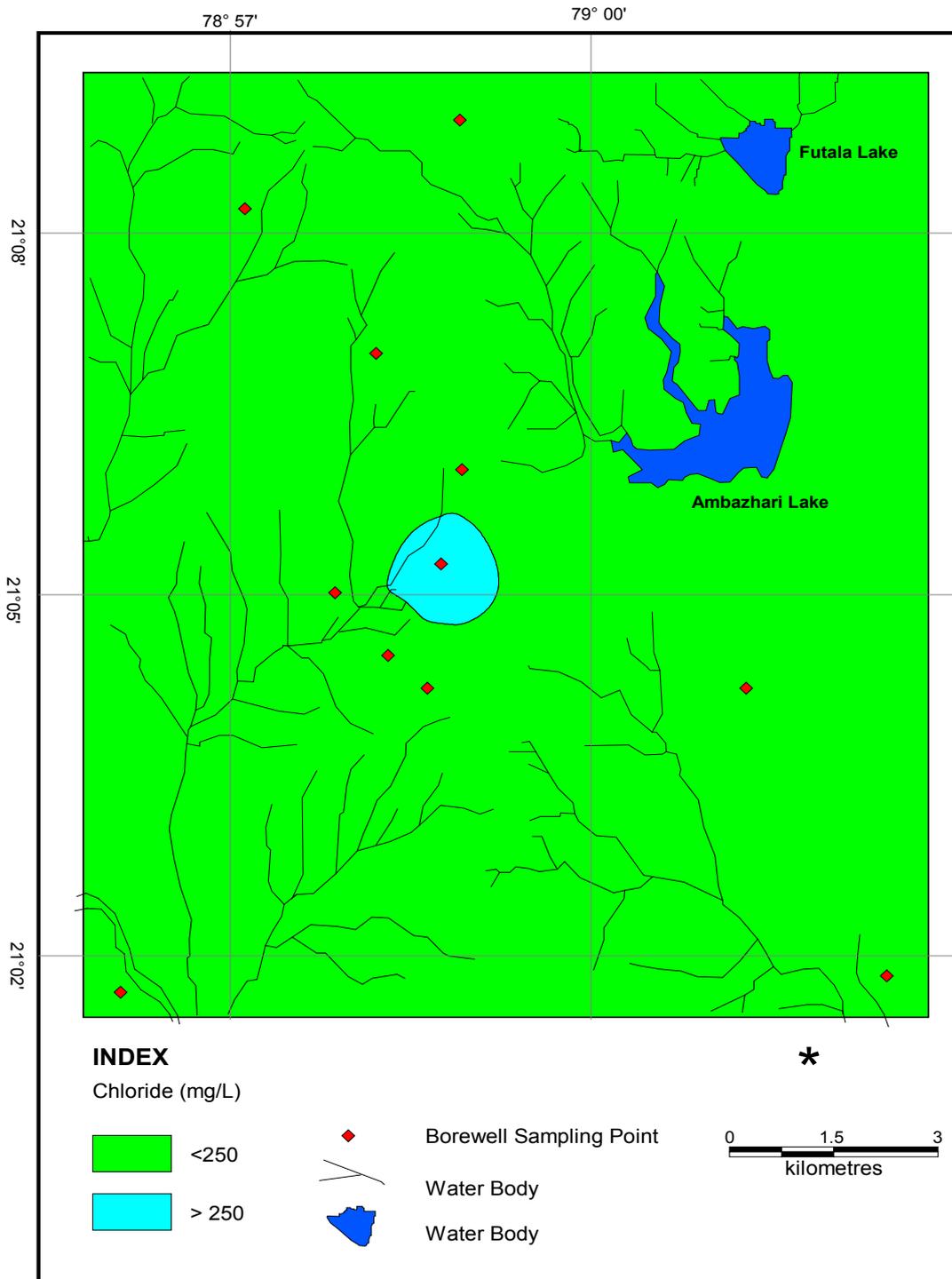### URBANISED PART OF NAGPUR DISTRICT, MAHARASHTRA

Figure 10. Distribution of Chloride in shallow and deeper aquifers

The graphical representation of the distribution of samples according to the WHO standards for major parameter is presented in Figure 11 (Shallow Aquifer) and Figure 12 (Deeper Aquifer). Their perusal indicates that the ground water quality in the area is mainly affected by Total hardness and Magnesium concentrations as both the parameters are above permissible limits of the WHO. These parameters are observed in excess, in both the shallow and deeper aquifers, it inferred that the concentration of these parameters have been altered due to percolation of pollutants even down to the deeper aquifer. However, the major health affecting constituents i.e., nitrate and fluoride concentrations reflecting the anthropogenic and geogenic pollution respectively. The values of Nitrate and Fluoride are within the permissible limits of the WHO in both the shallow and deeper aquifers.

The absence of Sulphate, Chloride (except one sample) and Nitrate, most probably reflects that the pollution due to the domestic sewage/waste water has so far not affected the ground water quality in the study area.
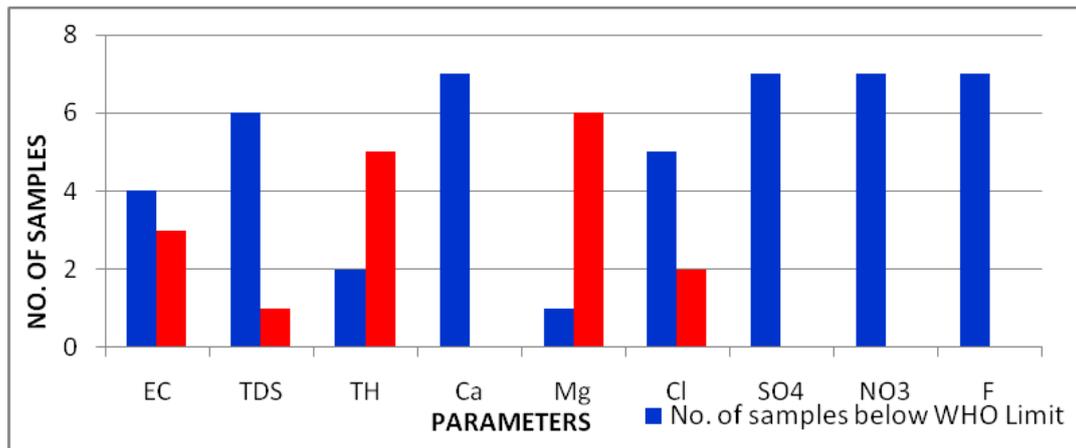
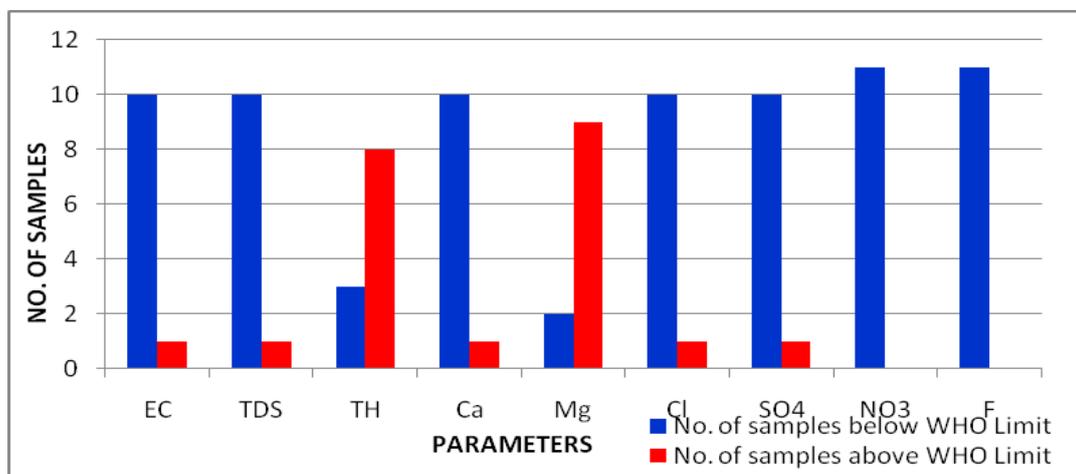**Figure 11.** Distribution of Samples in Shallow Aquifer as per WHO Standards

Figure 12. Distribution of Samples in Deeper Aquifer as per WHO Standards

Table 1. Analysis details of total 18 water samples of study area

Sr. No.	pH	EC	TDS	Alkalinity	Ca	Mg	TH	Na	K	HCO₃	NO₃	SO₄	Cl	F	CR	CA-I	CA-II	Ca-Mg Ratio

Sr. No.	pH	EC	TDS	Alkalinity	Ca	Mg	TH	Na	K	HCO_3	NO_3	SO_4	Cl	F	CR	CA-I	CA-II	Ca-Mg Ratio
Dug Well Samples (Shallow aquifer)																		
1	7.1	1262	794	284	120	63	558	31	2.9	346	3.8	61	170	0.56	0.88	0.54	0.22	1.16
2	7.4	1438	953	332	165	52	626	34	9.3	405	1.8	96	191	0.71	0.91	0.73	0.28	1.93
3	7.5	755	537	259	68	45	354	18	2	316	1.9	17	71	0.24	0.37	0.73	0.16	0.92
4	6.9	1644	998	310	144	86	712	32	9.7	378	1.5	94	254	0.5	1.21	0.48	0.26	1.02
5	7.3	1720	1141	392	116	133	835	29	6.3	478	2.9	96	282	0.54	1.04	0.33	0.16	0.53
6	7.3	1097	745	348	94	69	518	18	2	425	3.1	3	133	0.57	0.45	0.59	0.18	0.83
7	7.3	755	522	221	40	55	325	29	2	270	1.9	5	120	0.93	0.64	0.11	0.05	0.44
Minimum	**6.9**	**755**	**522**	**221**	**40**	**45**	**325**	**18**	**2**	**270**	**1.5**	**3**	**71**	**0.24**	**0.37**	**0.11**	**0.05**	**0.44**
Maximum	**7.5**	**1720**	**1141**	**392**	**165**	**133**	**835**	**34**	**9.7**	**478**	**3.8**	**96**	**282**	**0.93**	**1.21**	**0.73**	**0.28**	**1.93**
Average	**7.3**	**1239**	**813**	**306**	**107**	**72**	**561**	**27**	**5**	**374**	**2.4**	**53**	**174**	**0.57**	**0.78**	**0.50**	**0.19**	**0.97**
Bore Well Samples (Deeper aquifer)																		
8	6.5	1355	858	268	170	46	614	32	2.8	327	2.14	70	210	0.59	1.13	0.67	0.35	2.25
9	6.5	1317	868	287	108	75	577	31	2.4	350	1.61	118	183	0.82	1.09	0.43	0.17	0.87
10	6.9	1366	916	344	124	79	634	28	2	420	3.11	67.3	195	0.68	0.82	0.5	0.2	0.95
11	6.9	911	658	330	98	44	425	16	1.9	403	0.72	0	95	0.44	0.33	0.88	0.21	1.35
12	7.1	1238	827	298	72	89	545	30	2.9	364	1.03	90.8	178	0.44	0.95	0.25	0.1	0.49
13	7	1244	848	336	126	61	565	27	2.3	410	0.73	50.2	171	0.8	0.71	0.59	0.22	1.25
14	6.9	1287	858	424	106	86	617	13	1.7	517	1.6	0.3	133	0.62	0.36	0.71	0.18	0.75
15	7.1	1172	782	320	98	68	524	28	1.9	390	1.26	2.2	194	0.25	0.71	0.37	0.18	0.88
16	6.9	5010	2564	752	513	200	2102	170	3.1	918	0.12	427.4	332	0.67	0.99	1.04	0.26	1.56
17	7.1	719	511	264	50	58	363	14	1.8	322	0.86	2.5	62	0.49	0.28	0.61	0.12	0.52
18	7.2	844	590	292	30	73	374	23	1.5	356	0.88	3.8	102	0.75	0.41	0.08	0.02	0.25
Minimum	**6.5**	**719**	**511**	**264**	**30**	**44**	**363**	**13**	**1.5**	**322**	**0.12**	**0**	**62**	**0.25**	**0.28**	**0.08**	**0.02**	**0.25**
Maximum	**7.2**	**5010**	**2564**	**752**	**513**	**200**	**2102**	**170**	**3.1**	**918**	**3.11**	**427.4**	**332**	**0.82**	**1.13**	**1.04**	**0.35**	**2.25**
Average	**6.9**	**1496**	**934**	**356**	**136**	**80**	**667**	**37**	**2.2**	**434**	**1.27**	**76**	**168**	**0.6**	**0.71**	**0.56**	**0.18**	**1.01**

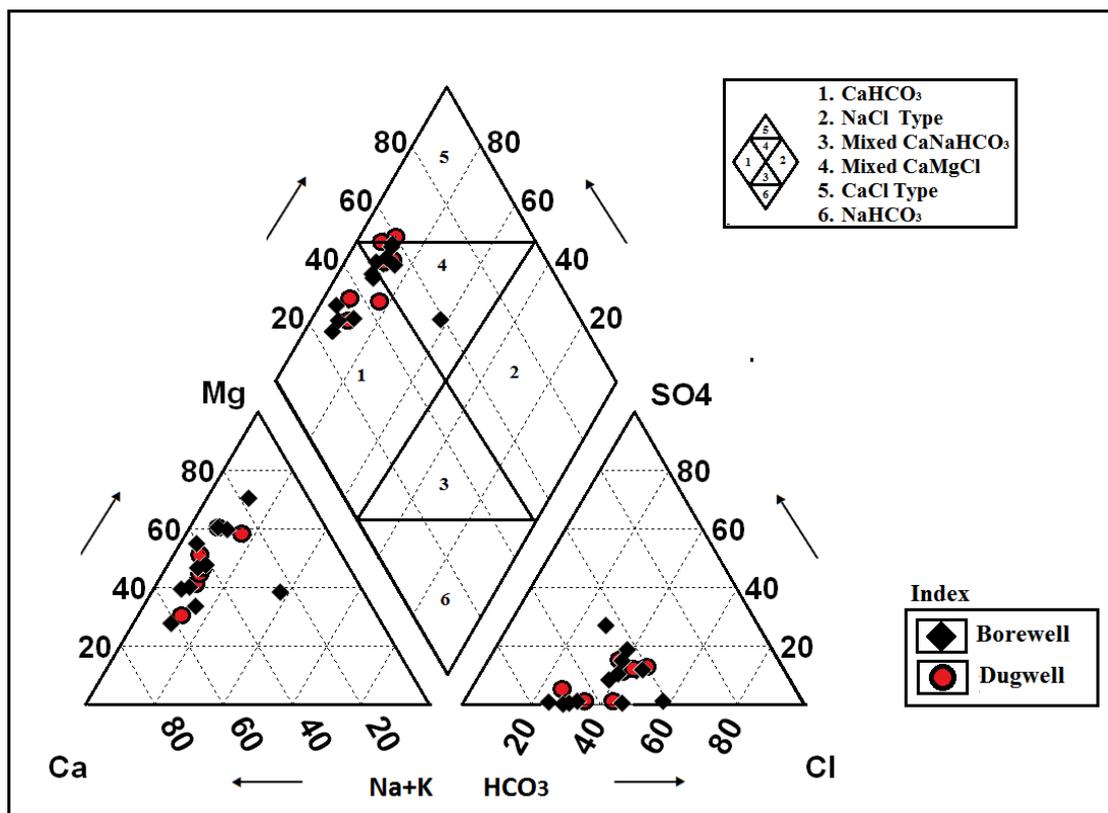(All values are expressed in mg/l, except pH and EC in μS/cm).

Figure 13. Piper's plot representing samples of the study area

3.2. Hydrochemical Facies (Hydrogeochemical Classification of Groundwater)

The ionic concentrations were plotted in Piper Trilinear diagram [30] to characterize geochemical nature of the groundwater in the study area. The cation and anion fields are combined to show a single point in a diamond shaped field, the inference is drawn on the basis of hydro-geochemical facies concept. It explains the variations or dominations of cation and anion concentrations. Piper diagram (Figure 13) detects that, the water samples fall under Ca-HCO$_3$ and Mixed Ca-Mg-Cl water type. Ca-HCO$_3$ facies reflect the prevalence of carbonates. In most of the samples, carbonate hardness exceeds 50%.

The alkaline earth (Ca^{2+} + Mg^{2+}) significantly exceeds the alkali (K$^+$ + Na$^+$) and weak acid (HCO$_3^-$) exceeds strong acid (Cl$^-$ and SO$_4^{2-}$), which leads mainly to Ca-HCO$_3$, mixed Ca-Mg-Cl and Ca-Cl type. With the exceeded values of Mg water samples also show temporary and permanent hardness. The hydrochemistry of the study area is controlled by basaltic terrain. The dominance of Ca-Mg-HCO$_3$ is due to rainfall recharge process, associated with low EC values; however, if the recharge is not predominant, it may lead to the Ca-Cl-HCO$_3$ type due to increased concentration of chlorides and sodium due to evaporation.

3.3. Correlation Matrix

The correlation analysis study involving statistical calculations was devised by Pearson [31]. The chemical composition of the groundwater is characterized by major cations and anions such as Ca, Mg, Na, K, Cl, SO$_4$, CO$_3$, and HCO$_3$. Table 2 and Table 3 represent the correlation coefficient matrices prepared for the pre-monsoon 2011. Weathering processes and anthropogenic inputs are the two main contributors for changing the geochemical composition of the groundwater [32].

In the present study, correlation of the analyzed water quality parameters and the following observations has been made for both dugwell and borewell. TA has a good correlation with HCO$_3$ (r = 1) for both borewells and dugwells. TH with Ca (r = 0.98 and r = 0.76), Mg (r = 0.94 and r = 0.82), SO$_4$ (r = 0.96 and r = 0.86), HCO$_3$ (r = 0.96 and r = 0.85). These relationships indicate existence of relationship between Ca, Mg, SO$_4$ and HCO$_3$ and these components contribute towards carbonate hardness and non-carbonate hardness in which, carbonate hardness is caused by Ca and Mg of HCO$_3$ and non-carbonate hardness is caused by Ca and Mg of Cl and SO$_4$. Positive Cl correlation with SO$_4$ (r =0.85 and r = 0.86) indicates the influence of evaporation, agricultural activities and poor drainage condition in the groundwater system [33]. A positive relationship is observed between Ca and HCO$_3$ (r = 0.92 and r = 0.61) and it shows that calcite dissolution may not be the source of Ca in the groundwater of the study area. Na-Cl relationship is often used to identify the mechanism for acquiring salinity in semi arid regions [2] (r=0.83 and r=0.65) anthropogenic interference in the groundwater system can probably be the reason.

The Ca is in good positive correlation with Na (r = 0.96 and r = 0.59) and Cl (r = 0.85 and r = 0.67) reflecting the influence of Ca and Na bearing minerals in addition to the sources of anthropogenic origin. Mg concentration is higher than Ca which may be due to the ferro-magnesium minerals.

Table 2. Correlation coefficient matrix for various hydro-geochemical aspects for dug wells (Shallow Aquifer)

	pH	EC	TDS	Alkalinity	Ca	Mg	TH	Na	K	HCO$_3$	NO$_3$	SO$_4$	Cl	F
pH	1													
EC	-0.52	1												
TDS	-0.4	0.99	1											
Alkalinity	-0.06	0.78	0.84	1										
Ca	-0.38	0.83	0.81	0.61	1									
Mg	-0.31	0.74	0.77	0.73	0.26	1								
TH	-0.43	0.99	0.99	0.85	**0.76**	**0.82**	1							
Na	-0.49	0.59	0.54	0.07	**0.59**	0.21	0.49	1						
K	-0.4	0.81	0.78	0.46	0.84	0.35	0.73	0.7	1					
HCO$_3$	-0.05	0.78	0.84	**1**	**0.61**	0.73	**0.85**	0.07	0.46	1				
NO$_3$	-0.08	0.08	0.09	0.29	-0.02	0.24	0.15	-0.15	-0.47	0.28	1			
SO$_4$	-0.4	0.91	0.89	0.56	0.86	0.53	**0.86**	0.75	0.89	0.56	-0.11	1		
Cl	-0.56	0.96	0.95	0.69	**0.67**	0.83	0.95	**0.65**	0.76	0.69	0.04	0.86	1	
F	-0.08	-0.06	-0.06	-0.2	-0.11	-0.07	-0.11	0.51	0.04	-0.19	-0.06	-0.07	0.09	1

Table 3. Correlation coefficient matrix for various hydro-geochemical aspects for bore wells (Deep Aquifer)

	pH	EC	TDS	Alkalinity	Ca	Mg	TH	Na	K	HCO$_3$	NO$_3$	SO$_4$	Cl	F
pH	1													
EC	-0.13	1												
TDS	-0.15	1	1											
Alkalinity	0.01	0.95	0.95	1										
Ca	-0.24	0.98	0.98	0.92	1									
Mg	0.07	0.94	0.94	0.93	0.87	1								
TH	-0.14	1	1	0.96	**0.98**	**0.94**	1							
Na	-0.08	0.99	0.98	0.92	**0.96**	0.93	0.98	1						
K	-0.42	0.64	0.64	0.43	0.66	0.51	0.63	0.64	1					
HCO$_3$	0.01	0.95	0.95	**1**	**0.92**	0.93	**0.96**	0.92	0.43	1				
NO$_3$	-0.42	-0.36	-0.33	-0.4	-0.31	-0.37	-0.34	-0.41	-0.14	-0.4	1			
SO$_4$	-0.23	0.97	0.97	0.86	0.94	0.91	0.96	0.97	0.75	0.86	-0.32	1		
Cl	-0.34	0.85	0.86	0.71	**0.85**	0.75	**0.84**	**0.83**	0.77	0.71	-0.01	0.85	1	
F	-0.35	0.18	0.19	0.15	0.17	0.18	0.18	0.17	0.08	0.15	0.1	0.27	0.15	1

3.4. Anthropogenic Inputs

Many studies reveal that variation in TDS in groundwater may be related to pollution [34,35]. The cations Ca and Mg concentrations generally increase with the increasing TDS and characteristically show a recognizably higher concentration in industrialized area [25]. Ca in dugwell samples shows higher concentration as compared to borewell samples (Figure 14 and Figure 15). The anthropogenic Ca in urban environment originates from various sources such as leather industry, waste water de-icing salts, domestic effluents, etc [36]. The increasing values of Mg from dugwell in study area seem to be derived from metal industry [37] (Figure 16 and Figure 17). The geochemical behaviour of calcium and magnesium is different from each other. Under natural condition, the concentrations of calcium may be higher than the magnesium and the ratio of Ca-Mg may be more than 1.0 but the concentration of calcium may get reduced during the circulation of water due to the precipitation and ion exchange [38]. The average Ca-Mg ratio of shallow aquifer in the area is to the tune of 0.97 and for deeper aquifer it is 1.01 which is almost normal for basaltic areas. It indicates that the concentrations of calcium and magnesium in ground water are very close to natural conditions and ground water contamination from anthropogenic sources has not yet affected the ground water quality.

The Na$^+$ concentrations show weak increasing trend in borewell with increasing TDS (Figure 18 and Figure 19) showing weathering of silicate minerals may be related to the anthropogenic sources such as sewage, household waste, engineering work effluents, de-icing road salt, etc [25,39].

Among anions, in particular chloride and bicarbonate ions show a good trend of increasing concentration with increasing TDS (Figure 20 and Figure 21) suggesting that they can be good pollution indicators. The general source of anthropogenic Cl in urban environment includes engineering work effluents, sewage, fertilizers, road slats, and de-chlorination of hydrocarbons [40,41]. HCO$_3$ concentration can be derived from leaky industrial and domestic sewage and also from the buried waste of old landfills (Figure 22 and Figure 23) [42]. The distribution of NO$_3$ is quite disperse and does not show any distinct relationship for anthropogenic control (Figure 24 and Figure 25). SO$_4$ show a good increasing trend with TDS (Figure 26 and Figure 27) which comes from industrial effluents and use of phosphatic fertilizer [37,43]. It should be noted that the groundwater from dugwell i.e., shallow aquifers shows a good increasing correlation with increasing TDS which reflects the increasing anthropogenic contamination among the shallow aquifers.
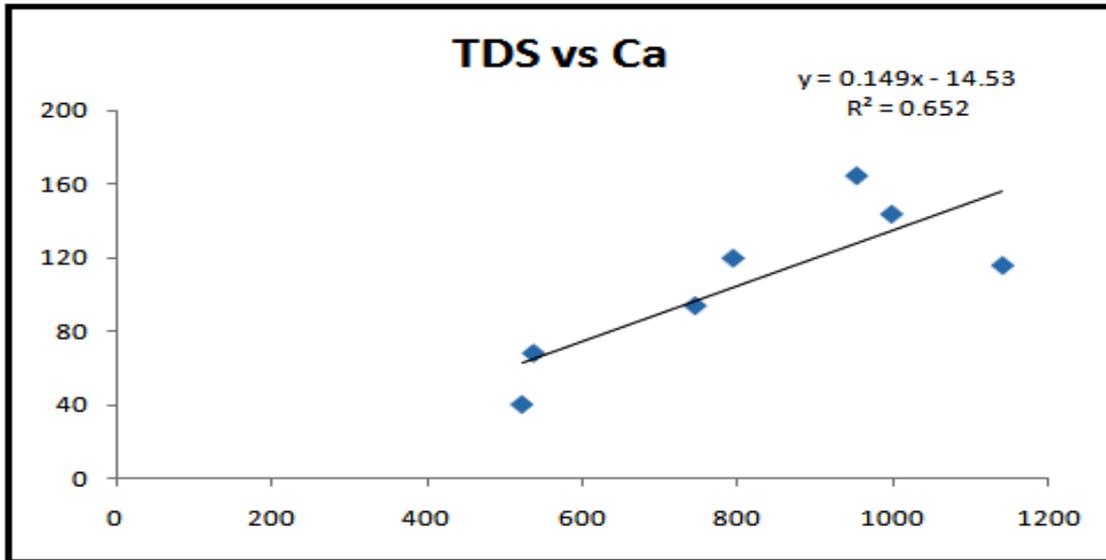
Figure 14. Ionic plots for TDS Vs Ca ions for dug well water samples of the study area
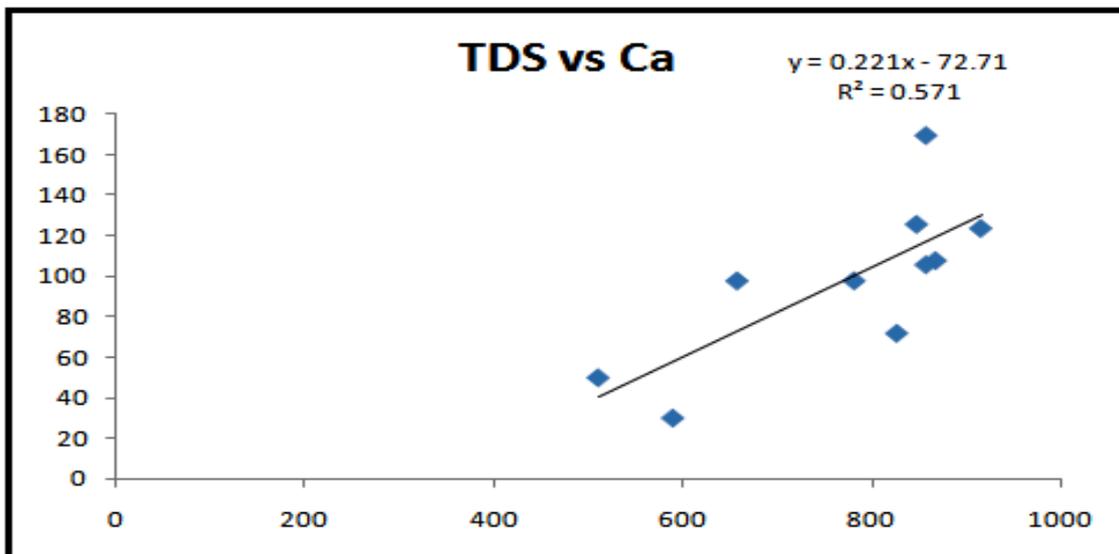

Figure 15. Ionic plots for TDS Vs ca ions for bore well water samples of the study area
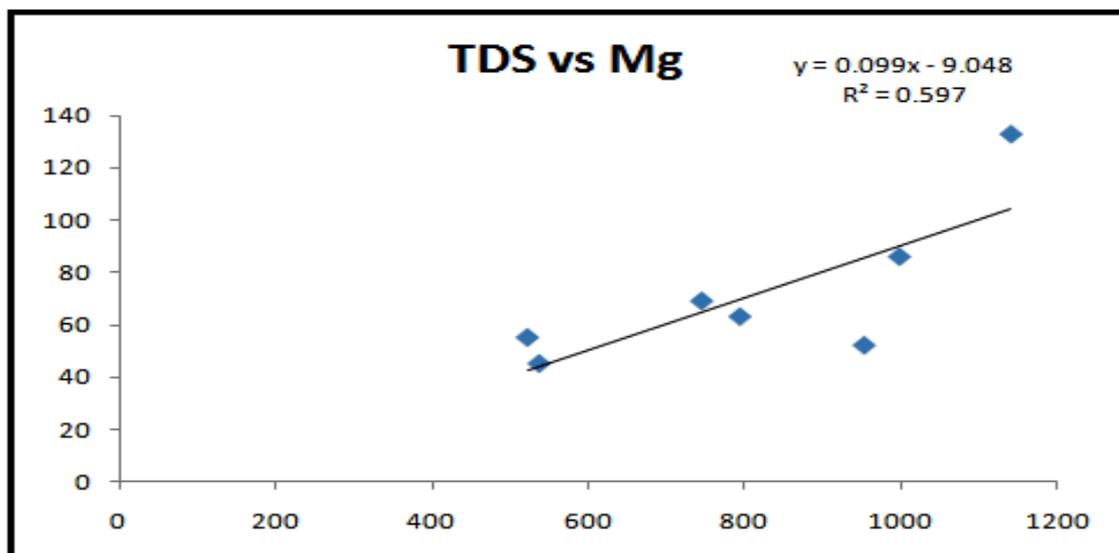

Figure 16. Ionic plots for TDS Vs Mg ions for dug well water samples of the study area
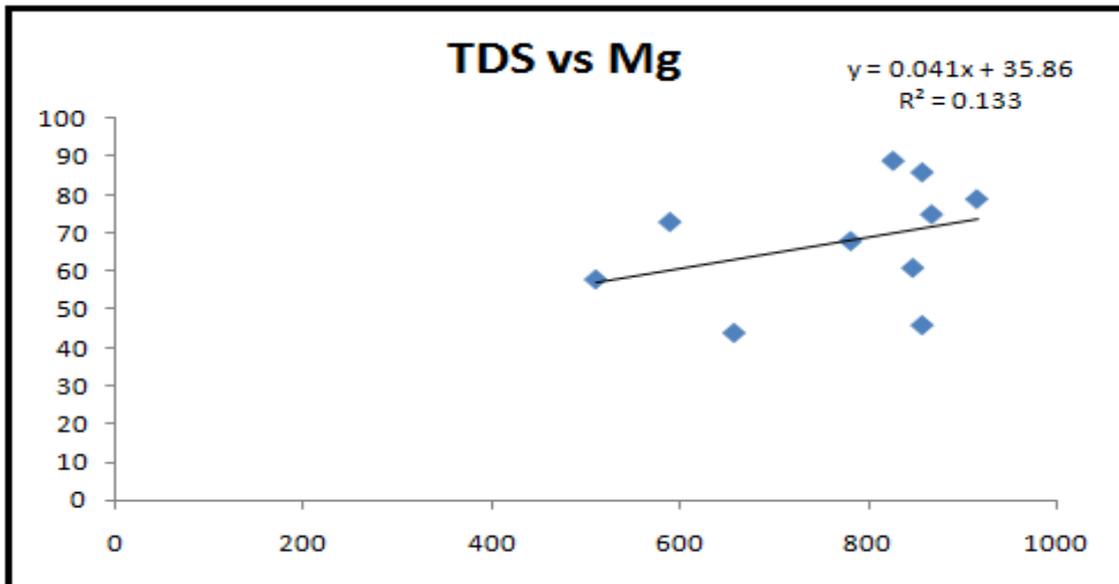
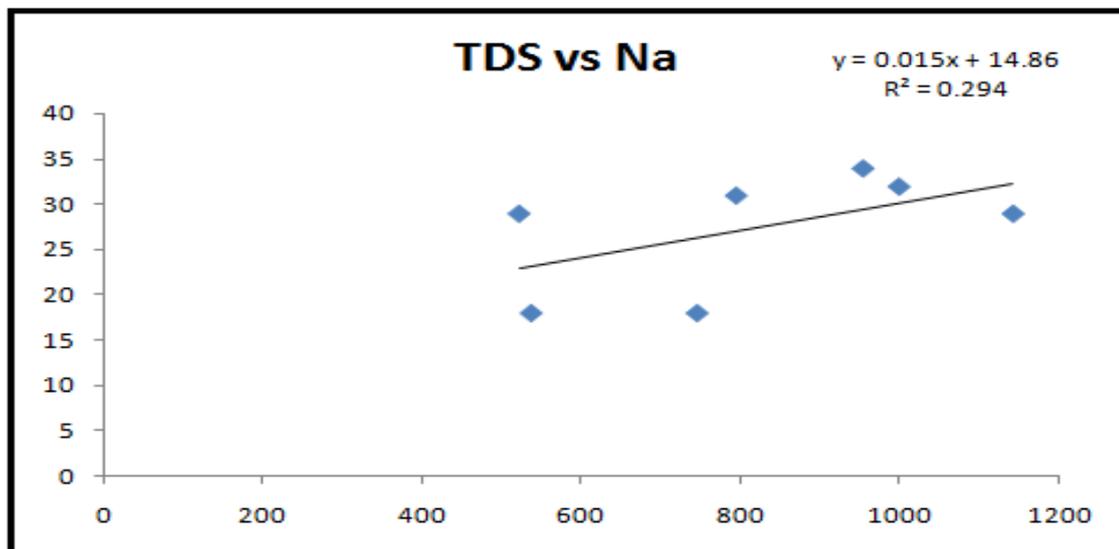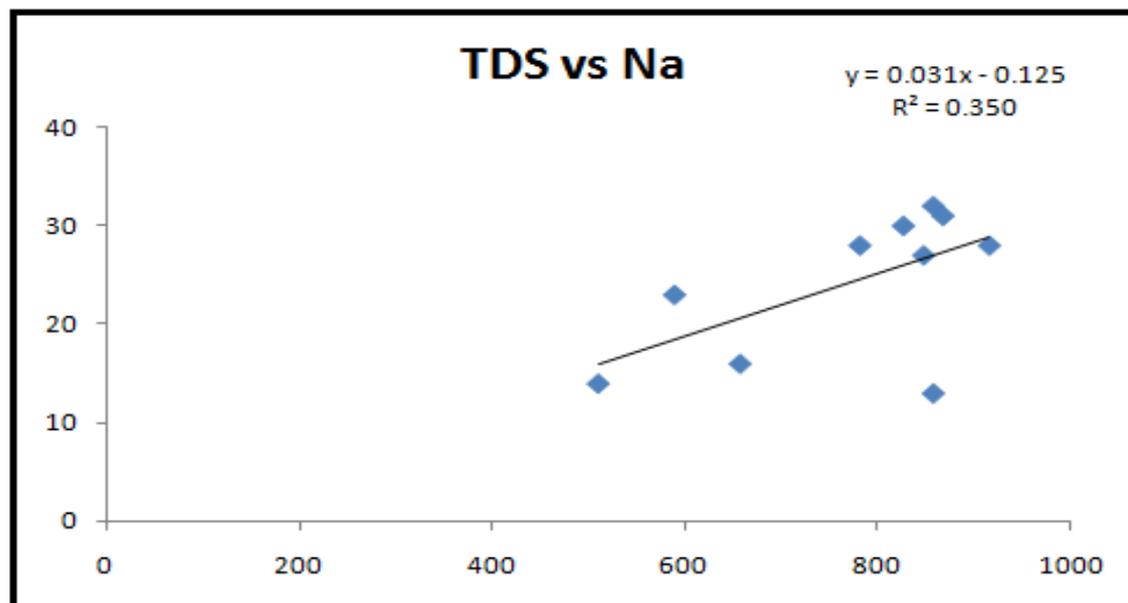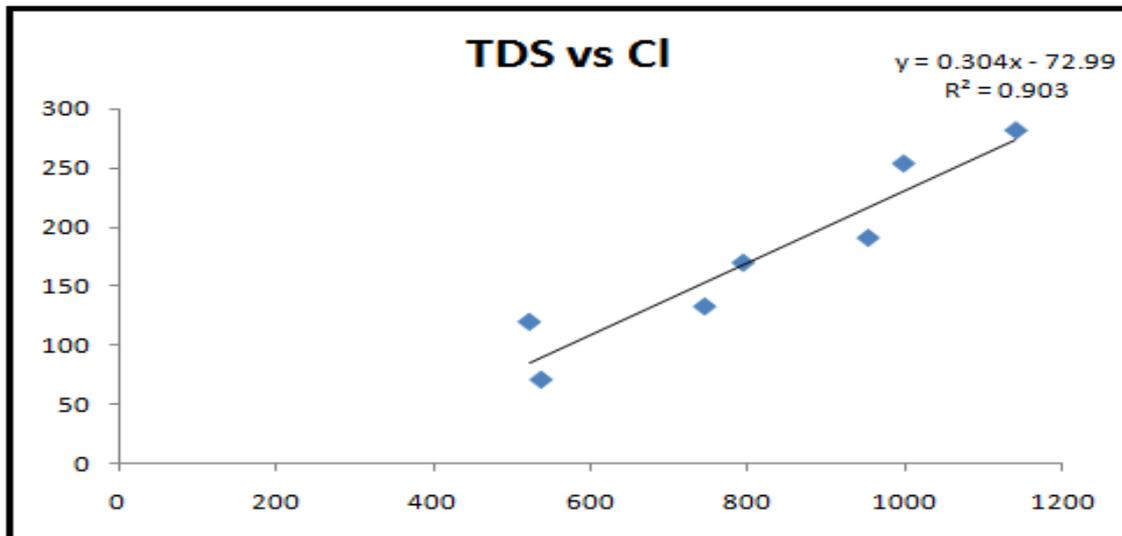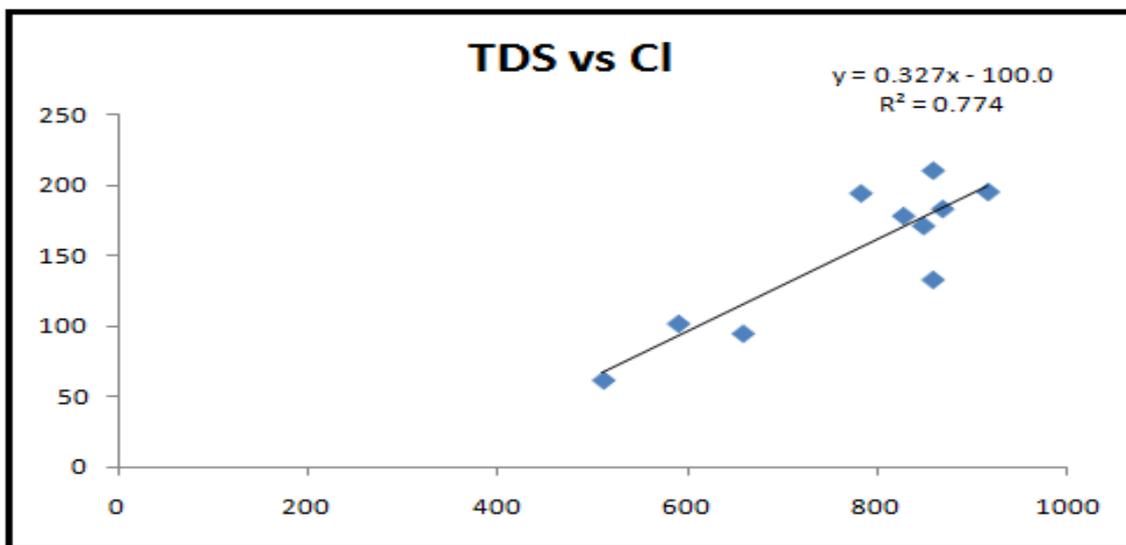**Figure 17.** Ionic plots for TDS Vs Mg ions for bore well water samples of the study area
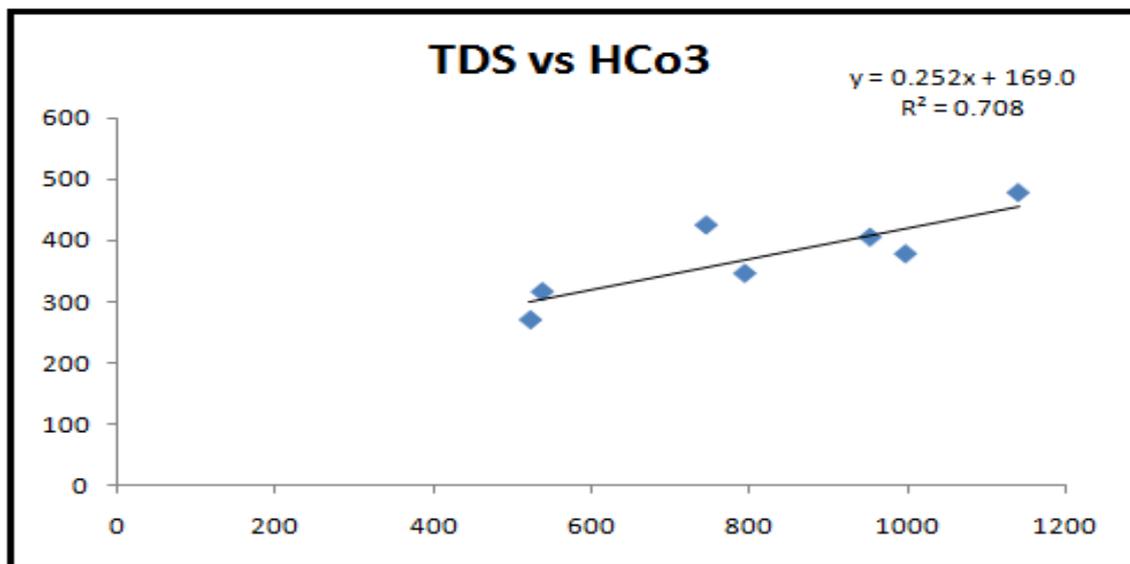

Figure 18. Ionic plots for TDS Vs Na ions for dug well water samples of the study area

Figure 19. Ionic plots for TDS Vs Na ions for bore well water samples of the study area

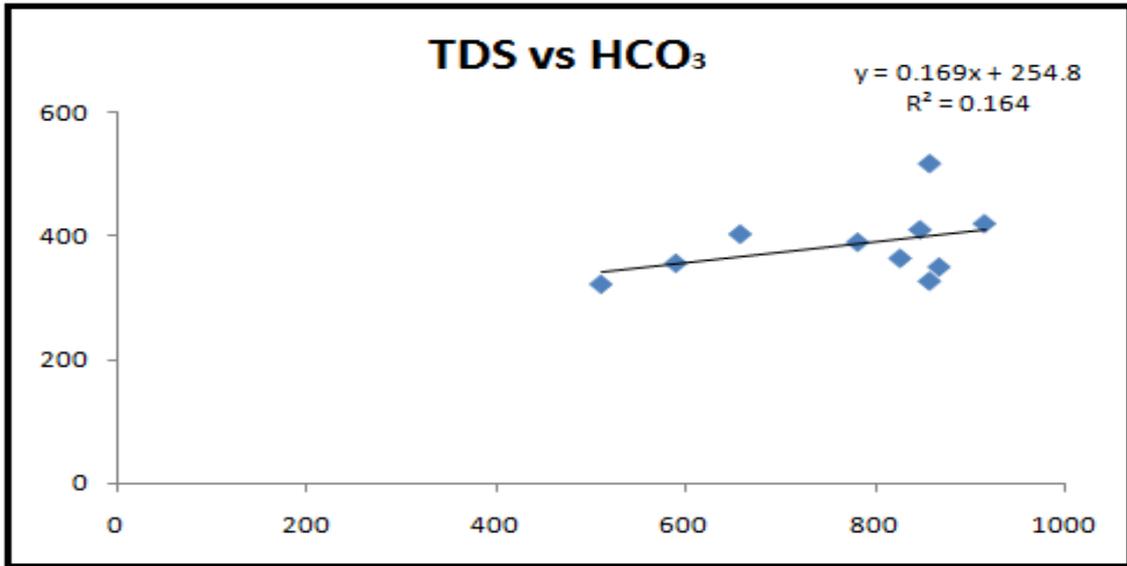**Figure 20.** Ionic plots for TDS Vs Cl ions for dug well water samples of the study area

Figure 21. Ionic plots for TDS Vs Cl ions for bore well water samples of the study area

Figure 22. Ionic plots for TDS Vs HCO_3 ions for dug well water samples of the study area

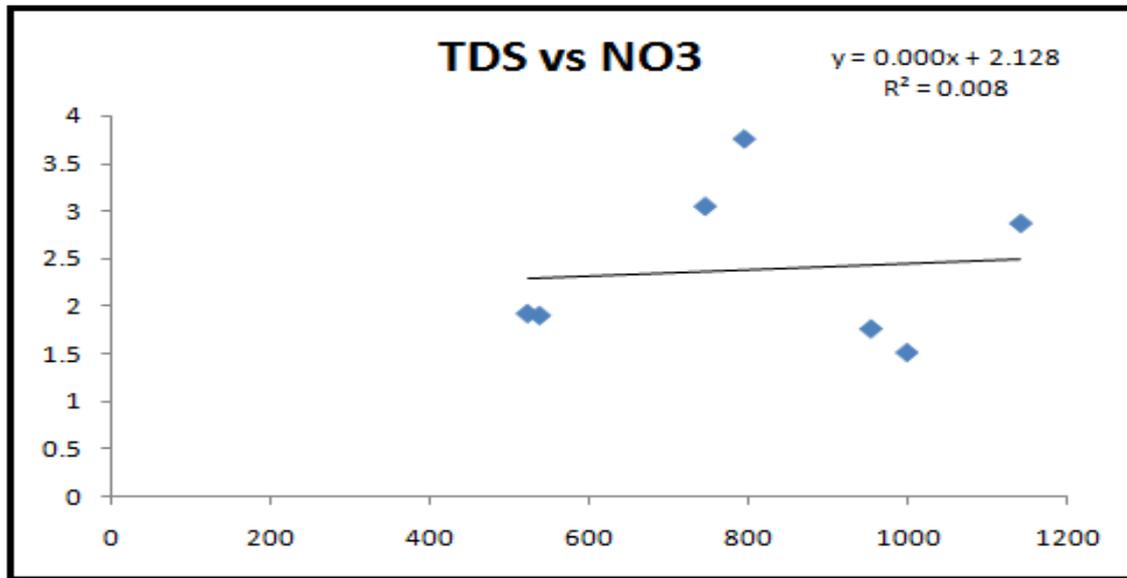**Figure 23.** Ionic plots for TDS Vs HCO$_3$ ions for bore well water samples of the study area

Figure 24. Ionic plots for TDS Vs NO$_3$ ions for dug well water samples of the study area

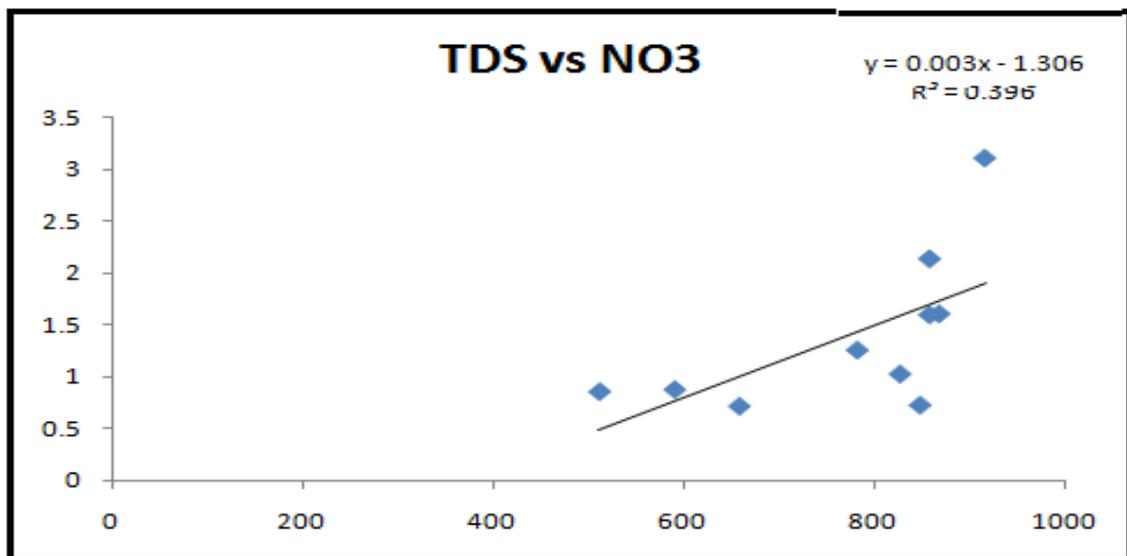**Figure 25.** Ionic plots for TDS Vs NO$_3$ ions for bore well water samples of the study area
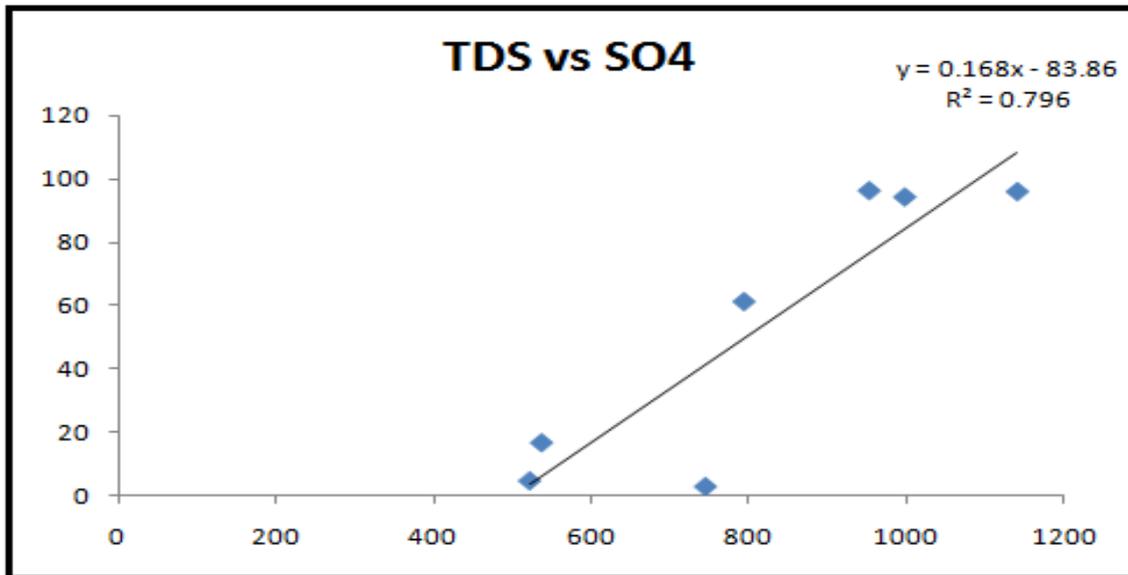
Figure 26. Ionic plots for TDS Vs SO$_4$ ions for dug well water samples of the study area
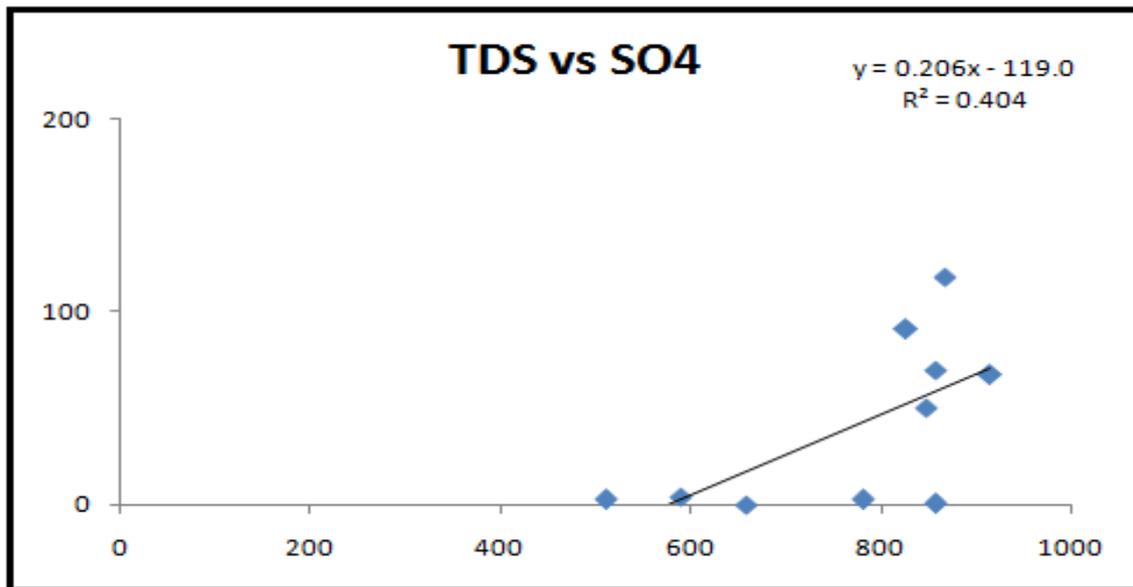

Figure 27. Ionic plots for TDS Vs SO$_4$ ions for bore well water samples of the study area

3.5. Ion Exchange (Chloro-alkaline Indices)

The Chloro-Alkaline Indices (CAI) give an idea of the chemical reactions in which ion exchange between the groundwater and aquifer environment takes place during its period of residence and movement [44,45,46]. The ion exchange between the groundwater and its host environment during residence or travel can be understood by studying the Schoeller index [44,45]. The Chloro-Alkaline Indices were computed by following formulas i.e., CA-I [(Cl$^-$ - Na$^+$ + K$^+$) / Cl$^-$] and CA-II [(Cl$^-$ - Na$^+$ + K$^+$) / (SO$_4^{2-}$ + HCO$_3^-$ + CO$_3^{2-}$ + NO$_3^-$)]. When Na$^+$ and K$^+$ ions in water are exchanged with Mg^{2+} and Ca^{2+} ions from the rocks, the positive value indicates Base Exchange reaction. Whereas, negative value indicates chloro-alkaline disequilibrium and the reaction is known as cation–anion exchange reaction. The positive chloro-alkaline indices for all the samples of study area (Table 1) confirm the base-exchange reaction (i.e., chloro-alkaline equilibrium) between the Na$^+$ and K$^+$ from the waters with Mg^{2+} and Ca^{2+} of the rocks from

aquifer material. Groundwater with a base-exchange reaction in which the alkaline earths have been exchanged for Na$^+$ ions (HCO$_3^-$ > Ca^{2+} + Mg^{2+}) may be referred to as base-exchange- softened water and those in which the Na$^+$ ions have been exchanged for the alkaline earths (Ca^{2+} + Mg^{2+}>HCO$_3^-$) may be referred to as base-exchange-hardened water [47].

3.6. Gibb's Diagram

The mechanism controlling chemical relationships of groundwater based on aquifer lithology has been studied by following the Gibbs diagram [48]. Three kinds of field are recognized in the Gibbs diagram namely, precipitation dominance, rock dominance and evaporation dominance. The Gibb's ratio for anions and cations i.e., Cl$^-$ / (Cl$^-$ + HCO$_3^-$) and Na$^+$ / (Na$^+$ + Ca^{2+}) of the water samples, when plotted against relative values of total dissolved solids, it is found that all the ground water samples fall under the rock dominance towards the zone of evaporation

(Figure 28), which reflect that the influence of weathering of different rocks produces different combinations of anions and cations in the groundwater [49]. Anthropogenic activities also influence the rock dominance by increasing Na and Cl and thus TDS which is responsible for spreading of the cations and anions from rock dominance towards zone of evaporation [50].

3.7. Wilcox Plot

To classify the groundwater suitability for irrigation, Wilcox [51] diagram was used to represent the sodium and salinity hazards. The Wilcox plot is a simple scatter plot of sodium hazard (SAR) on the Y-axis versus salinity hazard (conductivity) on the X-axis. The conductivity is plotted by default in a log scale.
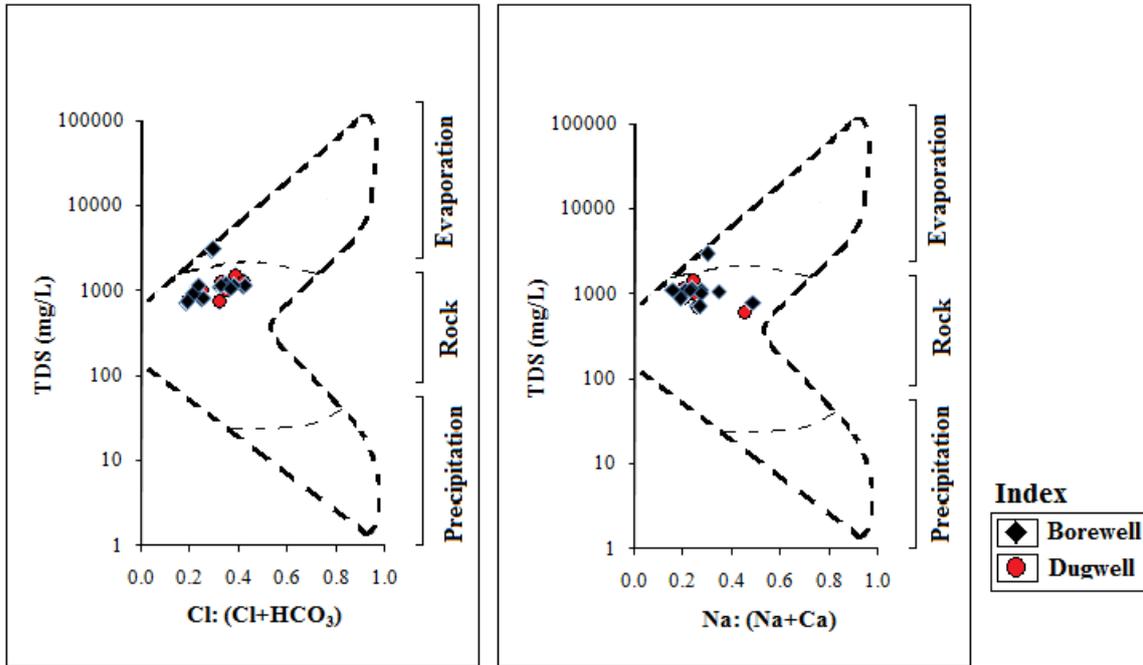

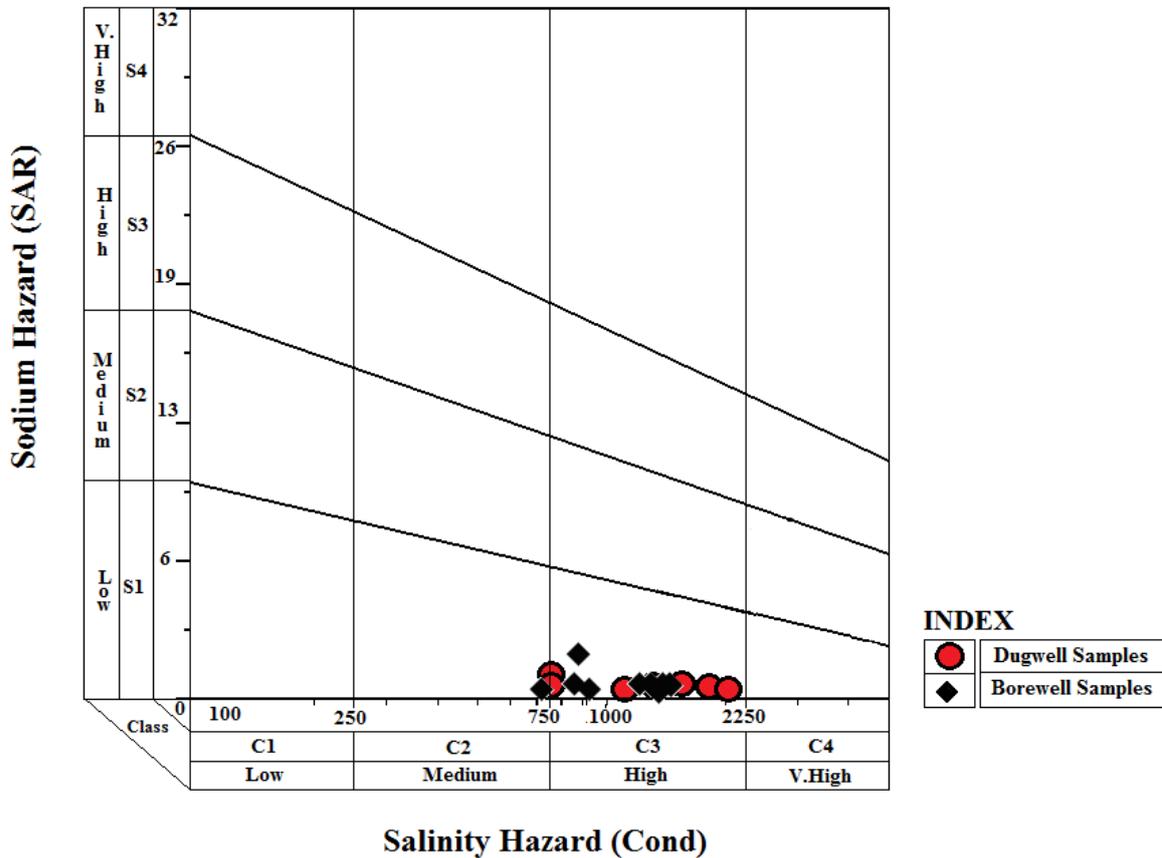**Figure 28.** Gibbs plot for the samples of the study area

Figure 29. US Salinity Laboratory Diagram for the study area

All the ground water samples from both dugwell and borewell fall under C_3-S_1 type with a few samples falling between C_3-S_1 and C_2-S_1 type (Figure 29). The samples falling under C_3-S_1 type indicate water of high salinity-low sodium type, which can be used for irrigation in almost all type of soils with little danger of exchangeable sodium [52]. The samples falling in C_2-S_1 type (medium salinity and low sodium) can be used for irrigation with most crops on most soils.

The sodium as alkali hazard in the use of water for irrigation is determined by the absolute and relative concentration of Sodium Absorption Ratio (SAR). The groundwater samples with SAR value < 10, 10-18, 18-26 and > 26 shows excellent, good, fair and poor quality of water for the irrigational purposes respectively. The average SAR of dugwell and borewell water samples of study area was 2.95 and 3.84. As per the classification of irrigation waters based upon SAR [53] the groundwater of the study area falls within the 'Excellent' class.

3.8. Corrosivity Ratio (CR)

It denotes the susceptibility of groundwater to corrosion and is expressed as ratio of alkaline earths to saline salts in groundwater. The effects of corrosion are losses in hydraulic capacity of pipes. The corrosivity ratio is defined by the formula;

$$CR = (Cl + SO_4) / 2(HCO_3 + CO_3)$$

Where all the ions are expressed in mg/L.

The CR values ≤ 1 is not corrosive, above 1 is corrosive and, hence, cannot be transported through metal pipes [54]. The CR value in groundwater of the study area ranged from 0.37 to 1.21 in dugwell and 0.28 to 1.16 in borewell (Table 1). It is observed that, total two (out of seven) dugwell samples and three (out of twelve) borewell samples show the higher corrosivity ratio.

4. Conclusion and Recommendations

The present study provides valuable information on the contaminants observed in the groundwater, their extent both spatial as well as vertical and probable causes of contaminants in the groundwater system of the study area. It also proves that the urbanization and industrialization affect groundwater quality to a considerable extent. The study suggests that, the chemical properties of groundwater are controlled by geochemical processes and anthropogenic activities. The hydrochemical analysis of groundwater reveals that, in major part of study area, the groundwater is hard to very hard, fresh and alkaline in nature. The spatial distribution of parameters such as TDS, total hardness calcium and magnesium with reference to the WHO standards indicates that the areas of contamination in shallow and deeper aquifers do not overlap and are occupying different areas. Thus lateral and vertical extent of the contamination has been deciphered.

Ground water potability in the study area is mainly affected by Total hardness and Magnesium concentrations in both the shallow and deeper aquifers. The exceeded values of Mg in water samples show temporary and permanent hardness in both type of aquifers. The excess of Mg indicates that, the ground water quality has been adversely affected most probably due to the presence of metal industries in the area.

The Piper diagram reflects Ca-HCO_3, mixed Ca-Mg-Cl and Ca-Cl type, suggesting that the groundwater hydrochemistry can also be controlled by anthropogenic inputs. Our study suggests that, Na is mostly derived from both natural as well as anthropogenic sources. The variation of TDS and its correlation with other ions supports the contribution of anthropogenic inputs to the groundwater contamination. Gibbs plot indicates dominance of rock water interaction in the study area. Base Exchange equilibrium is confirmed by the positive values of chloro-alkaline indices. Majority of the samples are good for irrigation in almost all type of soils with little danger of exchangeable sodium as they fall in very high salinity-low sodium field.

The absence of Sulphate, Chloride (except in one sample) and Nitrate, most probably reflects that the pollution due to the domestic sewage/waste water has so far not affected the groundwater quality in the area. The Ca-Mg ratio of shallow and deeper groundwater are very close to natural conditions and it suggests that groundwater contamination from domestic sewage sources has not yet affected the groundwater quality. However, high Total Hardness and Magnesium in both the phreatic and deeper aquifers may have been affected by industrial pollution and hence preventive steps should be taken up to protect these precious ground water resources. The study reveals that, the area of interest is more prone to groundwater pollution from industrial sources owing to its proximity to the industrialised centre and improper discharge of effluents.

Proper treatment and disposal of industrial effluents generated from the Hingna Maharashtra Industrial Development Corporation (MIDC) area needs to be prioritised. All the effluents should be treated in the Effluent Treatment Plant's (ETP's) before its disposal in the natural drainage. It must be ensured that, quality of the treated water is as per the norms of Central Pollution Control Board (CPCB) / Maharashtra Pollution Control Board (MPCB). Industries having unused storage lagoons in their premises should be identified and they should be filled with local clay or other impervious material to avoid further contamination of ground water due to natural recharge. Recycling and reuse of water need to be promoted and implemented by the industries.

Considering the ever looming perceptible threat of ground water pollution through sewage, it is imperative to improve the local sanitation system in the study area by installing small sewage treatment plants and then releasing the treated sewage effluent into the Nag River or local streams.

Rain water harvesting should be promoted in both urbanised and industrialised areas, and it should be made mandatory particularly in industrial areas, so that, the ground water recharge is able to dilute the contamination in ground water over the period of time. This will also help in augmenting the ground water resources of the area. Capacity building through training and public awareness programs (on hygiene, water handling and system maintenance) should be available to the local people in the area.

All the drinking water sources are to be checked for their chemical constituents before consumption and unfit sources may be discarded. Regular monitoring of the ground

water quality from both shallow and deeper aquifer in view of sustained urbanisation and industrialisation in the area is required to be followed to assess the ground water quality from time to time and suggest suitable remedial measures.

Acknowledgements

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