

# Geochemical Evaluation of Groundwater in the Mandvi Taluka of Surat, India

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## Abstract

The quality of water is a vital concern for mankind since it is directly linked to human health. The present work is carried out with an objective to assess and map the spatial variability in the groundwater quality parameters in Mandvi Taluka, Surat district Gujarat, India. A total fifty-seven representative groundwater samples from different bore wells and hand pumps from Mandvi Taluka has been collected and analyzed for major cation and anions with fluoride concentration for the pre-monsoon and post-monsoon seasons. Groundwater in the region is found alkaline, with presence of bicarbonates in nature and very hard. Weathering and leaching of  $F^-$  bearing minerals under the alkaline conditions favors the high  $F^-$  concentration. Presence of low total hardness, low calcium hardness, high chlorides, high bicarbonates and some anthropogenic factors such as intensive and long-term irrigation, heavy use of fertilizers are the supplementary factors to further enhance the  $F^-$  concentrations in the groundwater. Moreover, GIS spatial distribution maps give better visual image to understand the spatial distribution pattern to overlook better conclusion.

## Keywords

Groundwater Quality, Fluoride, Spatial Distribution Map

## 1. Introduction

Fluoride though occurs in minor quantities in natural water; due to its impact on human health it gained significant interest. Fluoride in drinking water has both benefit and drawbacks on human health. Low quantity of  $F^-$  is good for the formation of dental enamel and mineralization of bone [1] [2]. Excessive amount of  $F^-$  in groundwater can cause a negative effect on human body such as fluoride content greater than 1 mg/l causes dental fluorosis, bones get stiff and

brittle bone/joints and results in inability to walk or stand straight and crippling fluorosis, whereas when  $F^-$  concentrations is above 3.0 mg/l causes skeletal fluorosis [3] [4] [5]. It was early in the 1986 when fluorosis has been marked only in 13 states of India, 15 in 1992, 17 in 2002 and now it has been increased up to 19, signifying the endemic level of fluorosis. Thus, this health problem has reached up to alarming level in the country. About 80% of the diseases in the world are due to the poor quality of drinking water [5]. Recent studies in 2006 have indicated that around 200 million people including 6 million children suffer from fluorosis from 25 nations have health risks because of high fluoride concentration in groundwater, causing fluorosis [6]. This is due to ingestion of fluoride beyond permissible limit *i.e.*, >1.5 mg/l. Fluoride epidemic has been reported mostly in granite and gneissic geological formation of different states in India [7]. Moreover, most of the states have the reached the endemic level due to the higher concentration of fluoride in the groundwater [8] [9] [10] which is having the similar problem as in the study area.

Geospatial technology in the context of today's need is the state of the availability and providing service to the end users. The spatial variability and the GIS maps can be used for monitoring of ground water quality and effective decrease of contamination related threats can be achieved. However, GIS includes managing, compiling and analyzing the spatial data. With the help of tools such as Arc GIS Spatial Analyst extension analyzing and modeling of spatial data can be done. In addition, interpolation tools can be used for a set of sample points describing changes in population, landscape, or environmental parameters to visualize the pattern, trend, and variability in the observed data along the surface. Thus, variability in the data like lithology, morphology and their characteristics can be extrapolated along the geographic surface. Thus, it can be said that facility to generate surfaces from the observed sample data makes the interpolation tool more efficient, useful and powerful tool in GIS.

Number of studies has been carried out in this context such as Srinivasa-moorthy in 2009 have carried a detailed geochemical study for pre monsoon (PRM) and post monsoon (POM) seasons and identify quality of groundwater to determine its suitability for domestic use in Salem district of Tamilnadu, India [11]. Mohan in 2000 has evaluated the chemical characteristics of groundwater and the suitability of groundwater for irrigation and domestic uses in and around the industrial area of Naini district, Allahabad [12]. Subba Rao in 2003 describes hydro geochemistry and quality of groundwater to prepare baseline information on groundwater resources in the developing urban area of Guntur, Andhra Pradesh [13]. Groundwater classification was attempted by Ahmed in 2002 and Bathrellos in 2008 explained the suitability of groundwater for drinking purpose and public health [14] [15]. Similar type of studies have been done in different parts of the world by Stamatis in 2006; Wen in 2008, and Anku in 2009 and Joseph in 2012 evaluated fluoride contamination in groundwater during pre-monsoon and post monsoon period using remote sensing and GIS techniques in Virudhunagar District, India [16] [17] [18] [19]. Kumar and Kumar

have studied the impact of fluoride on human health and analyze the fluoride concentration in groundwater, their resources in kishanganj district, Bihar, India [20]. This research has been carried out to examine the causes and sources of high fluoride concentration in the ground waters and to determine the safe and unsafe locations in the study area with respect to fluoride concentration. Thus, this study helps to understand and analyze spatial distribution pattern which reflects the geochemical controls on its occurrence and this helps in judging important decisions in groundwater management in the study area.

## 2. Material and Methodology

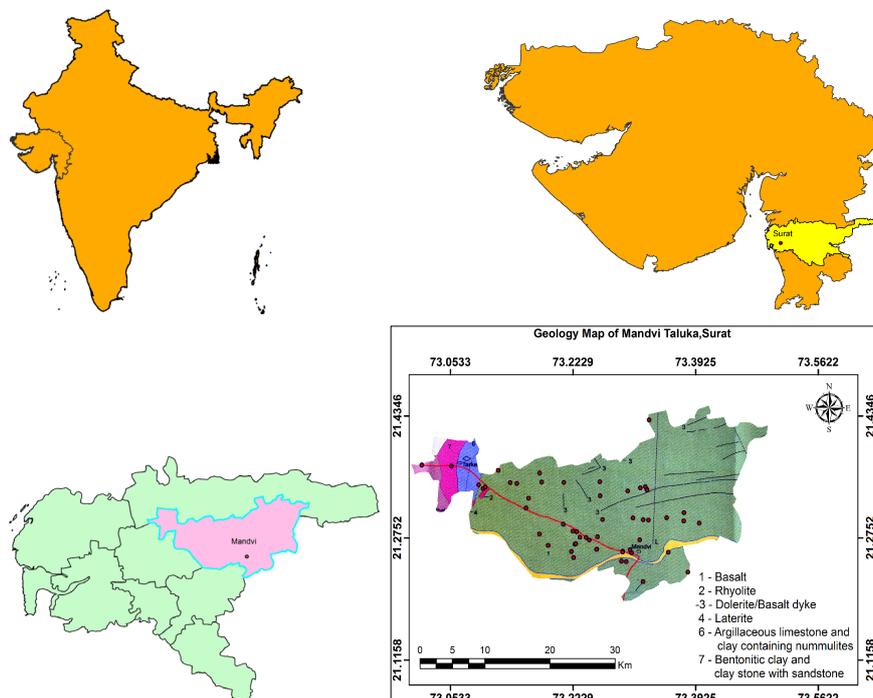
### 2.1. Study Area

The study area is having Latitude and Longitude of Mandvi Taluka are 21.15°N 73.18°E and having geographical area 829.02 sq. Km experiences a semiarid climate. An average annual rainfall is about 1701.8 mm. Temperature in the study area varies from 30°C to 42°C. Alluvial plains situated towards the central parts of the district are characterized by flood plains of the Tapi, Kim and Purna rivers. Topography of the study area is normally plain with gentle slope towards the west.

It comprises rocks like Basalt, Rhyolites, Dolerite/Basalt dyke, Laterite, Argillaceous limestone and clay containing nummulites and clay, friable sandstone, pebbly sandstone, a conglomerate which are remarked as fluoride -bearing minerals areas in Mandvi, Surat. Large thick basaltic aquifers are found in the north-eastern, eastern and south eastern parts of the area. Study area is having black clayey to loamy soil which is due to the presence of basaltic lava in the study area. At some places there is change in the color of soil which is due to the presence of high iron content at places. Soil at piedmont sloppy area ranges from shallow-moderately deep, moderate -severely eroded and non-calcareous in nature. Texture of the soil is varies from silt clay loam to clay loams. Besides, the hydro geological area is basically managed by the geological setting, rainfall distribution, circulation facilities and movement of water which further associates with major and minor porosity of the lithological units to forms the aquifers. **Figure 1** shows geology map of the study area with sample locations. Fluorspar ( $\text{CaF}_2$ ), Cryolite ( $\text{Na}_3\text{AlF}_6$ ), Fluor-apatite ( $\text{Ca}_3(\text{PO}_4)_2\text{Ca}(\text{FCl})_2$ ) are some of the major and common fluoride-bearing minerals; of which Fluorite ( $\text{CaF}_2$ ) is the chief carrier of fluoride found in granite, granite gneisses and pegmatite [21] [22]. Moreover, there are major excavation projects of minerals (*i.e.* Lignite, Bauxite, Fluorspar, Limestone, Bentonite, Manganese, Silica sand and Ball clay) near Tadmashwar in Mandvi.

### 2.2. Sampling and Analysis

Fifty-seven groundwater sample locations (Hand pump and Bore well) during summer season (PRM) and post monsoon (POM) were taken to analyze the fluoride contamination and other parameters in groundwater at Mandvi Taluka, Surat. To find complete representation for the fluoride contaminated location



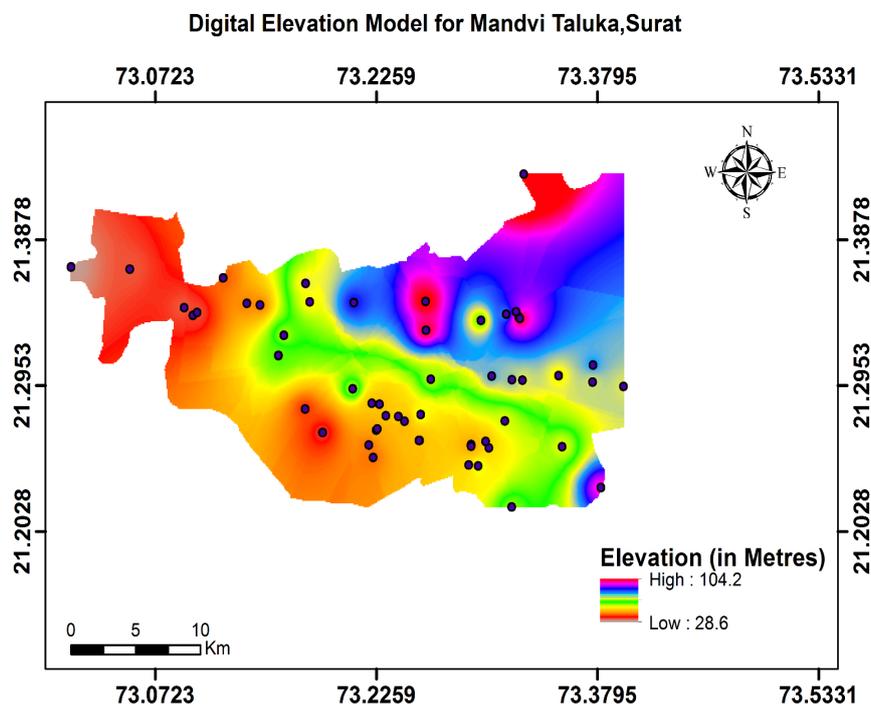
**Figure 1.** Geology map of the study area. Source: District Resource Map Surat District, Gujarat, GSI.

and intensity of fluoride in groundwater care has been taken to collect the sample from the same locations only. The Samples were taken using acid washed plastic container to avoid unpredictable changes in characteristic as per standard procedures [23]. Details of sampling locations along with their latitude and longitude were fixed using a hand-held GPS. Portable instrument has been used for the determination of pH (Hydrogen ion concentration), electrical conductivity (EC) and temperature. However, SPANDS method is used for the determination of fluoride, gravimetric method for TDS and titration method for calcium hardness, magnesium hardness and bicarbonates followed by standard method and procedures [23].

### 3. Results and Discussions

**Table 1** represents summarized statistical data for the groundwater Samples from Mandvi Taluka, Surat. **Figures 3-13** show spatial distribution maps for  $F^-$  and various other parameters for the PRM and POM seasons. **Figure 2** shows Digital Elevation Model for Mandvi Taluka, Surat. Digital elevation model and geology of study area shows that there is higher elevation towards northeastern side with some slope and basaltic dykes towards the western and eastern part of the study area.

The pH shows strength of water to react with acidic and alkaline materials. The alkaline conditions of groundwater are more favorable for solubility of fluorine bearing minerals and Fluoride solubility in groundwater is strongly influenced by the pH. However, during alkaline medium, desorption of fluorine



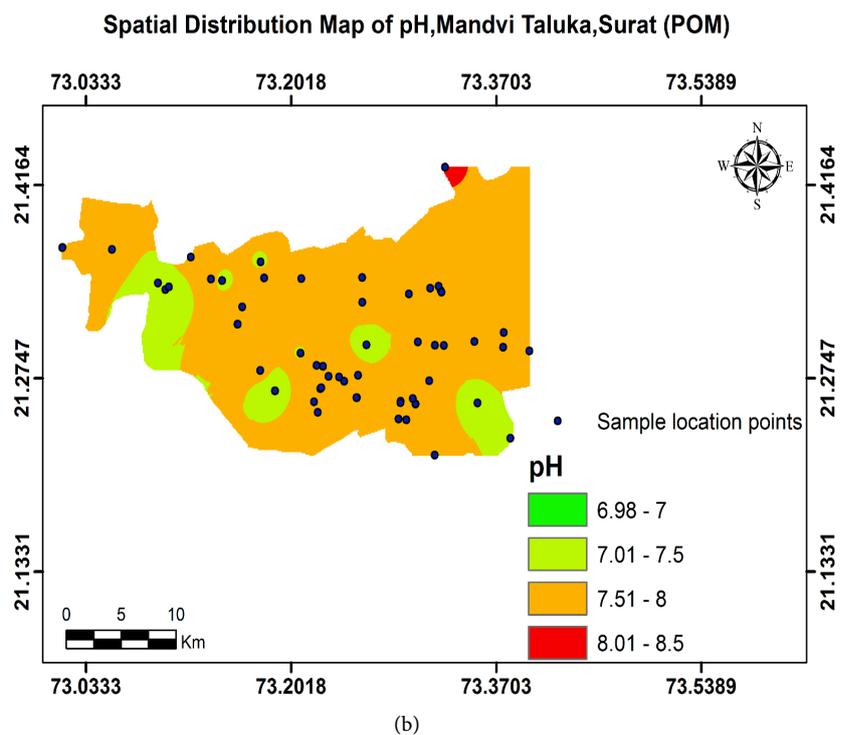
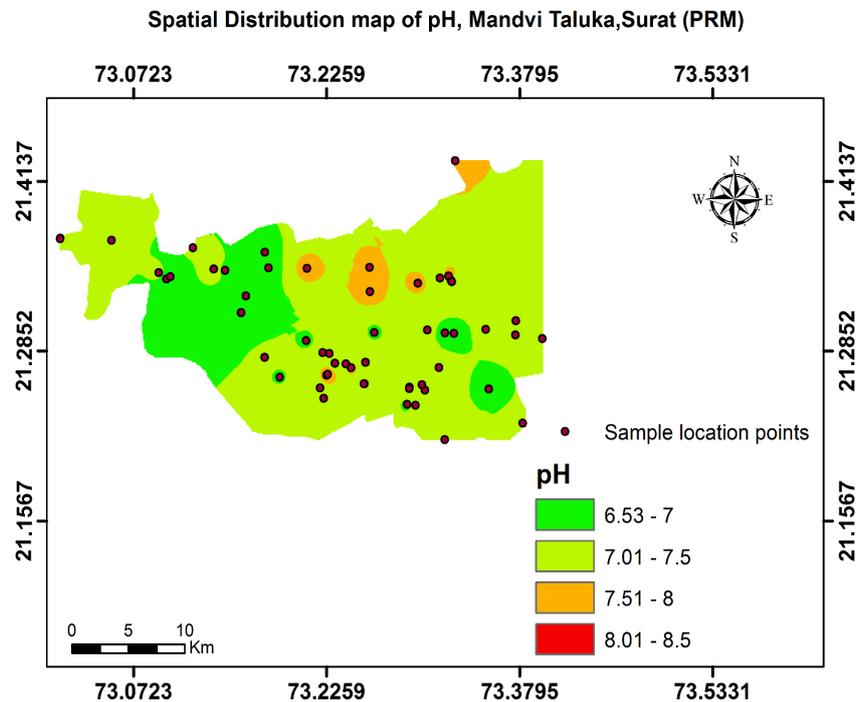
**Figure 2.** Digital elevation model, Mandvi Taluka, Surat.

**Table 1.** Summarized statistical data for the GW Samples from Mandvi Taluka, Surat..

Chemical Parameters	Pre-monsoon				Post-monsoon				BIS- (10,500, 2012)		WHO (1984)
	Min	Max	Mean	Std. Dev.	Min	Max	Mean	Std. Dev.	DL	PL	
pH	6.53	7.95	7.19	0.32	6.98	8.15	7.66	0.27	6.5 - 8.5	NG	-
Temp	26.5	31.5	29.30	1.12	26.6	31.2	29.34	1.06	-	-	-
EC	204	3971	942.65	624.05	280.0	3890.0	937.94	578.88	500	2000	-
TA	160	656	343.66	114.26	200.0	706.0	341.08	106.65	200	600	-
TH	116.2	993.5	307.86	147.8	109.2	991.6	323.52	152.96	200	600	500
Ca <sup>2+</sup>	28.6	186.2	70.17	30.39	28.0	190.0	70.21	32.69	75	200	75
Mg <sup>2+</sup>	7.8	144.7	32.14	24.55	2.4	138.6	38.33	26.87	30	100	150
F <sup>-</sup>	0.17	4.17	0.98	0.78	0.18	4.98	0.91	0.91	1.0	1.5	1.5
TDS	192	3360	696.56	479.54	250	3500	801.47	581.63	500	2000	500
HCO <sub>3</sub> <sup>-</sup>	195.2	800.3	4.16	136.81	207.0	800.0	419.24	130.49	200	600	-
SO <sub>4</sub> <sup>2-</sup>	16	70	31.96	8.95	13	136	43.61	16.95	200	400	400
NO <sub>3</sub> <sup>-</sup>	1.1	36.0	11.41	9.10	1.6	84.2	32.78	14.26	45	NG	45
Cl <sup>-</sup>	24	250	65.05	47.62	43	330	107.21	60.95	250	1000	-

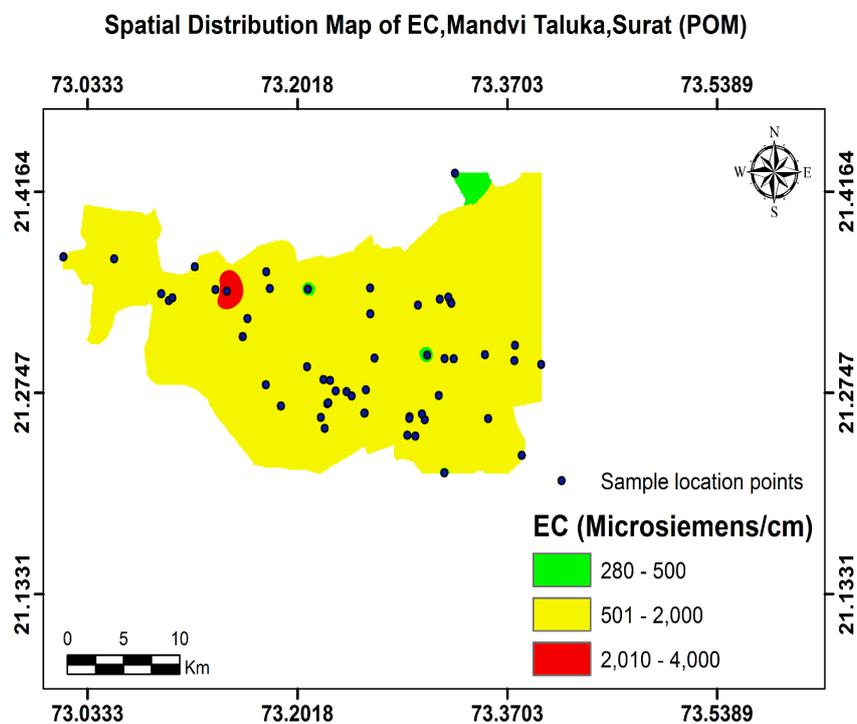
All the anion and cation values are shown in mg/l, except Temperature in °C & EC in µS/cm at 25°C; NG-No Guidelines, DL-Desirable Limit, PL-Permissible Limit.

takes place which ultimately favors the solubility of fluoride dissolution activity [24] [25] and [26]. In addition to this, pH is controlled by carbon dioxide, carbonate and bicarbonate equilibrium. Moreover, pH of water is affected by the

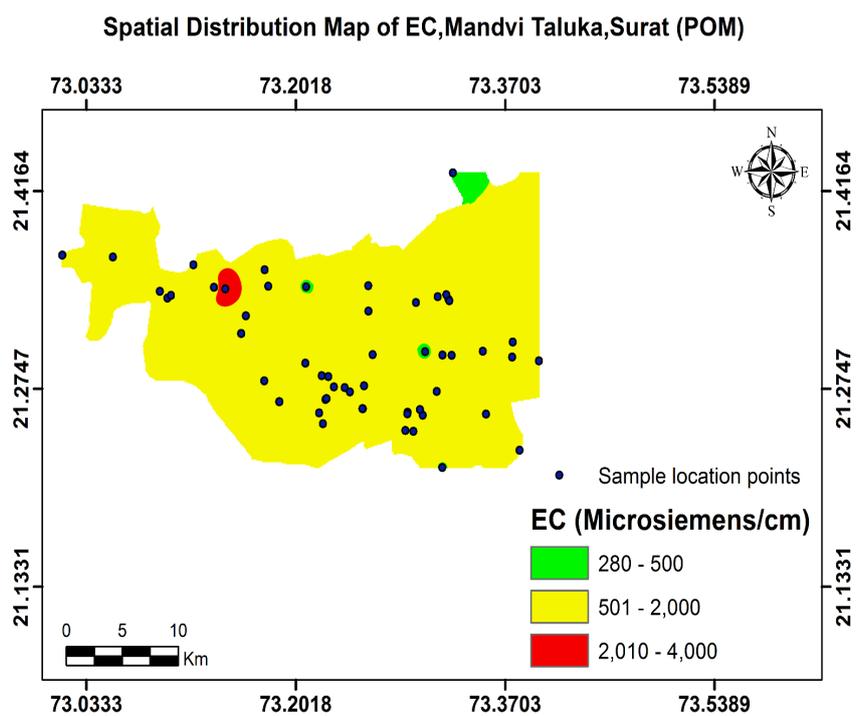


**Figure 3.** (a) Spatial Distribution map of pH (PRM); (b) Spatial Distribution map of pH (PRM).

combination of  $\text{CO}_2$  with water which forms carbonic acid. In present study maximum samples are alkaline in nature during both the seasons. The spatial distribution map of pH shows (Figure 3(a) & Figure 3(b)) during POM in the



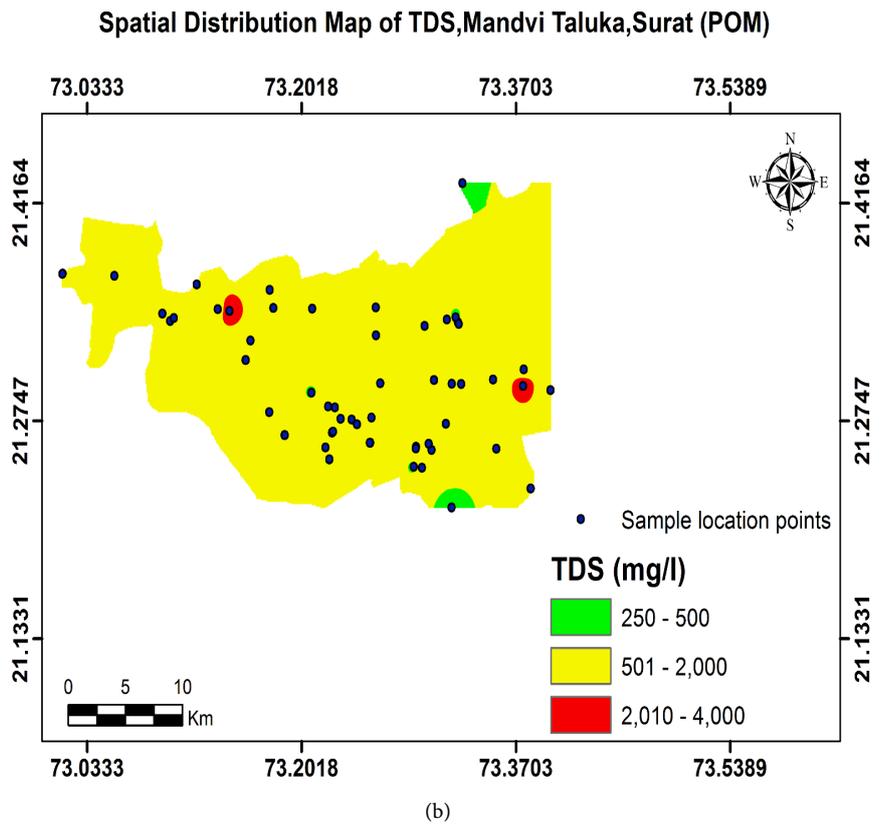
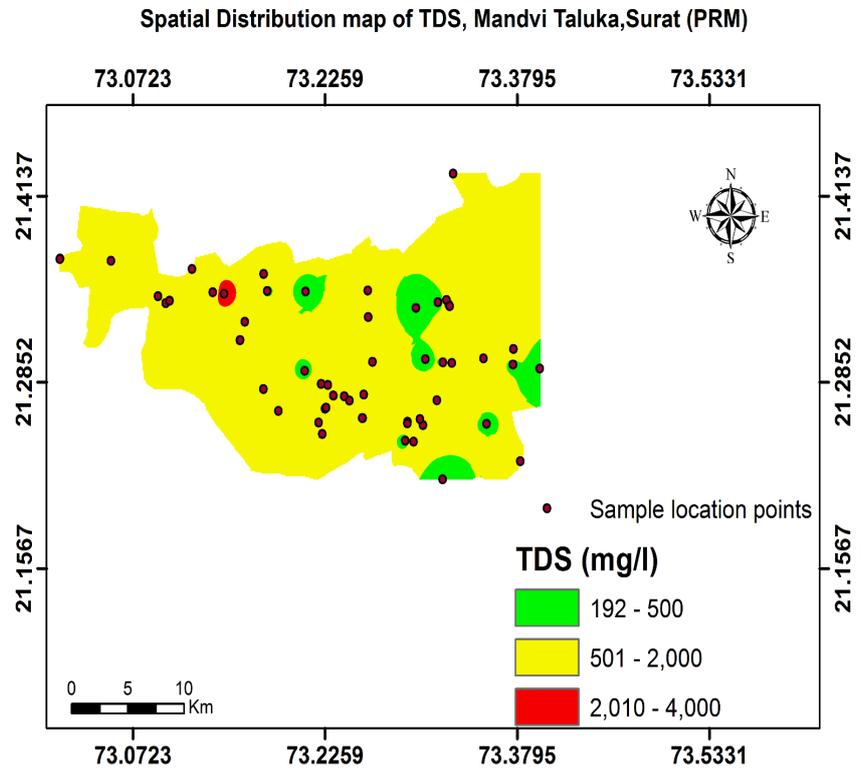
(a)



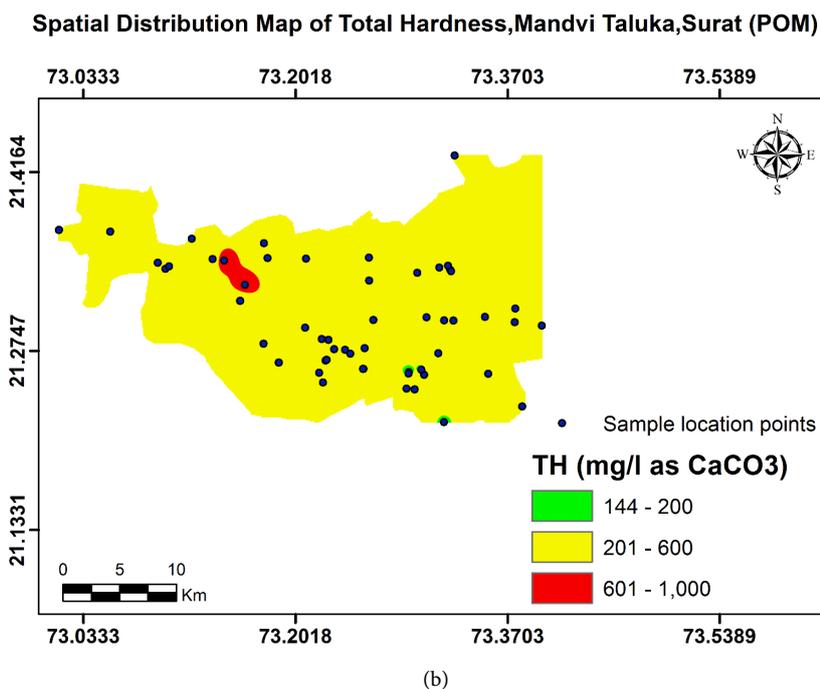
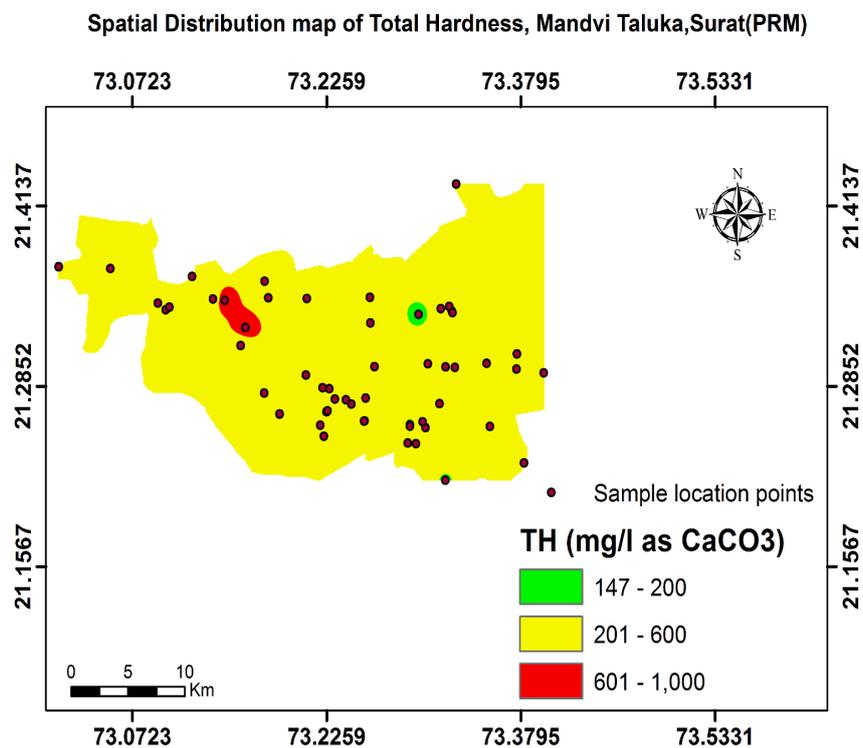
(b)

**Figure 4.** (a) Spatial Distribution map of EC (PRM); (b) Spatial Distribution map of EC (POM).

NE part of the study area, there is a change in the color distribution as compared to PRM, and in the remaining area there is a slight increase in the pH which

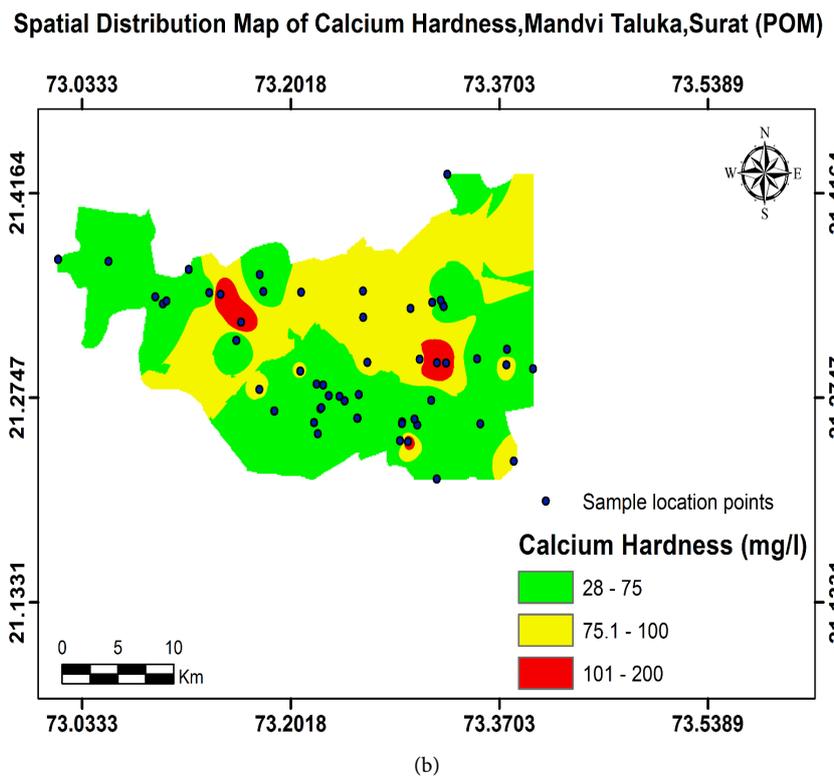
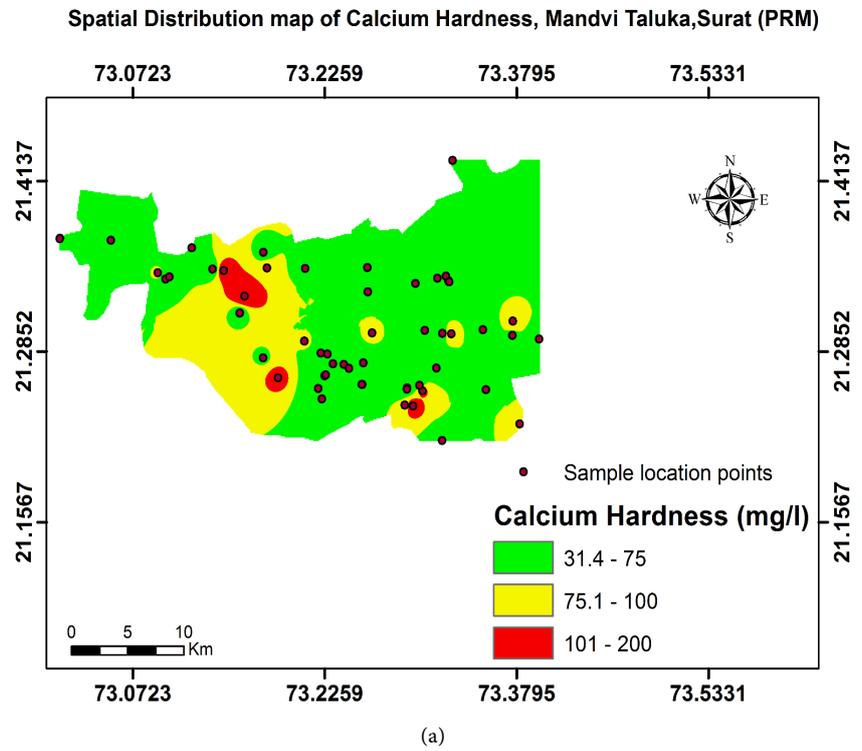


**Figure 5.** (a) Spatial Distribution map of TDS (PRM); (b) Spatial Distribution map of TDS (POM).



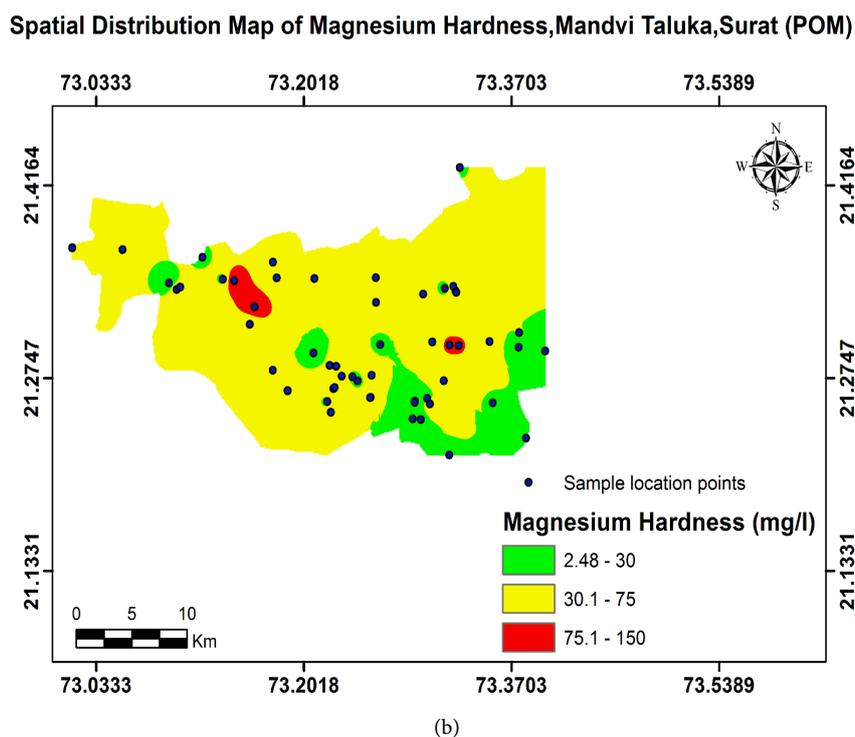
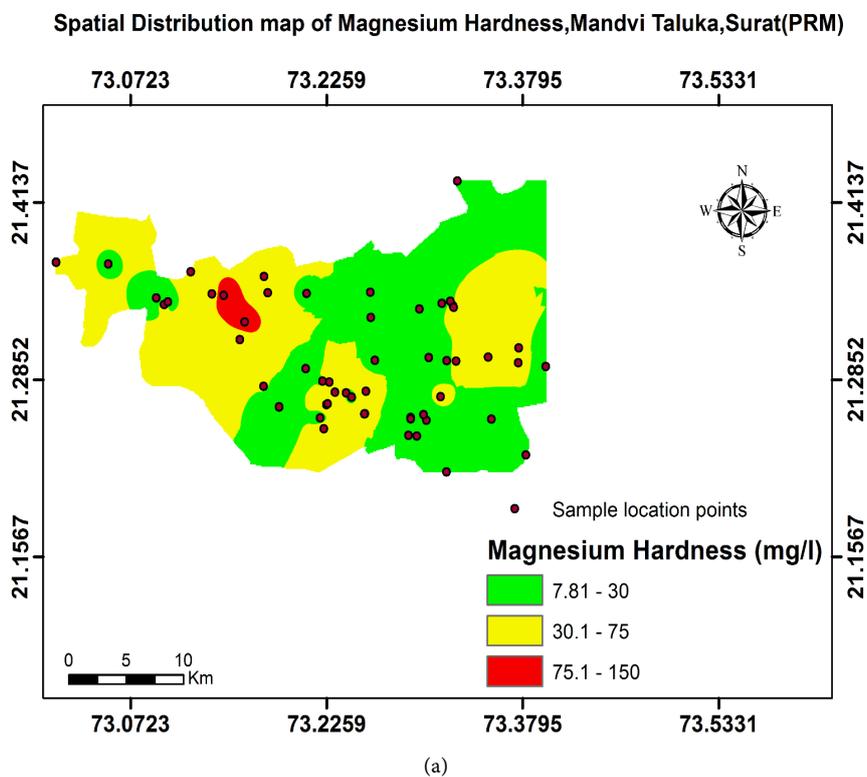
**Figure 6.** (a) Spatial Distribution map of TH (PRM); (b) Spatial Distribution map of TH (POM).

shows the variations in the pH is due to the rainfall effect. Thus from the spatial distribution map of pH it can be said that study area indicates and favors an alkaline pH conditions.



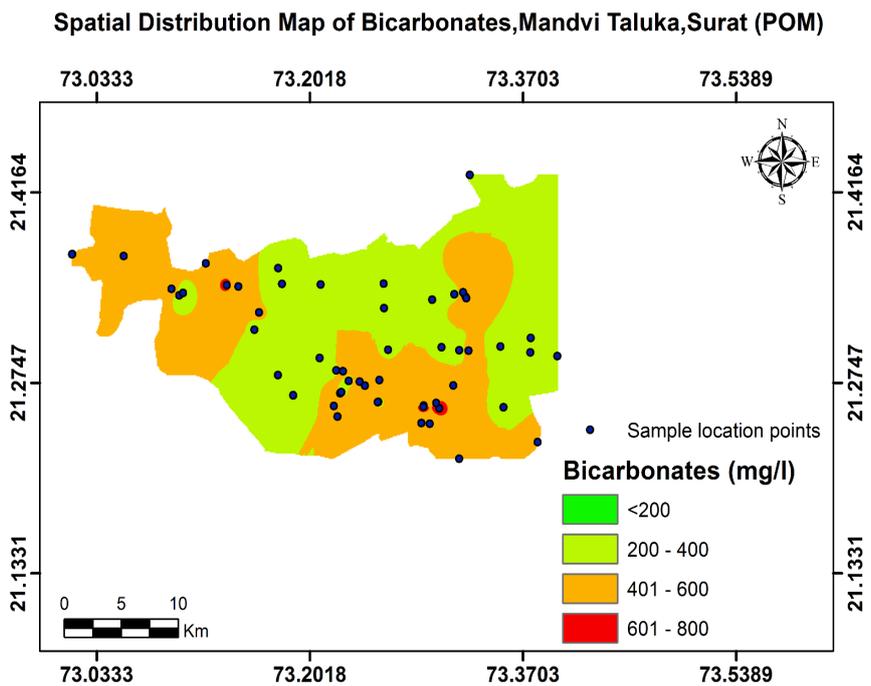
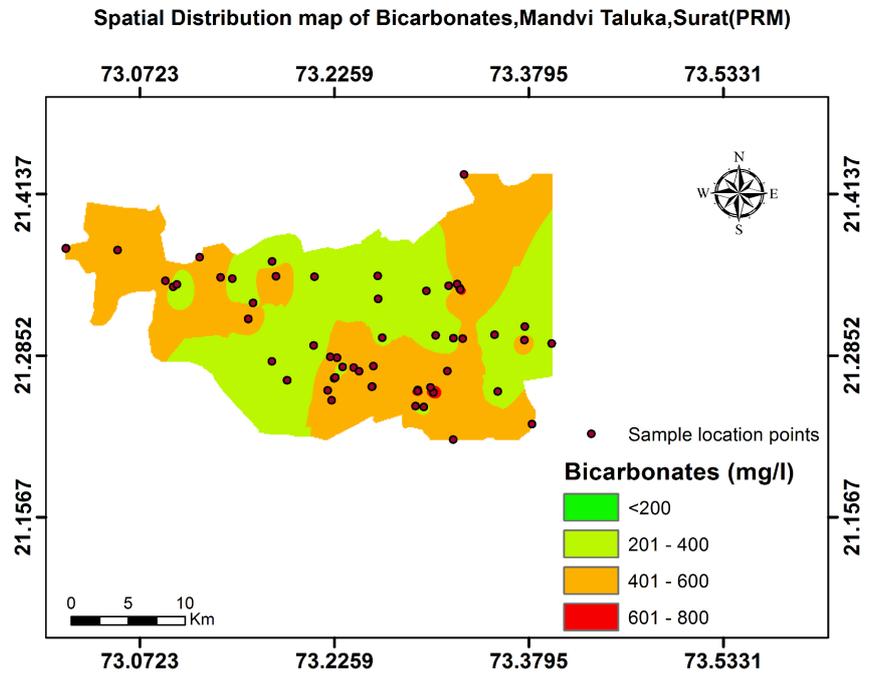
**Figure 7.** (a) Spatial Distribution map of CaH (PRM); (b) Spatial Distribution map of CaH (POM).

The EC (Electrical conductivity) is a measure of an ability to conduct current so that the higher EC indicates the enrichment of salts in the groundwater. The



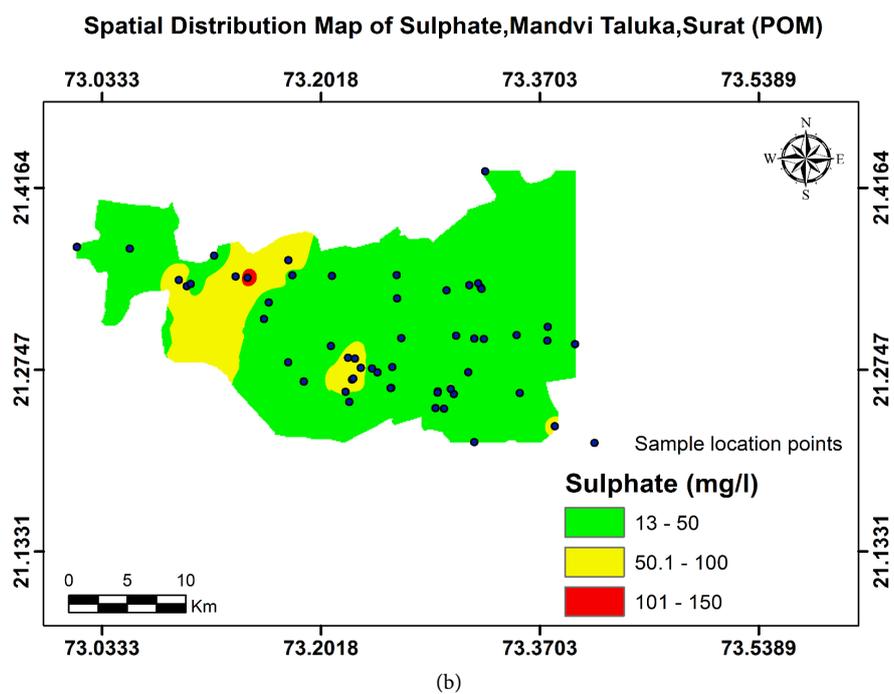
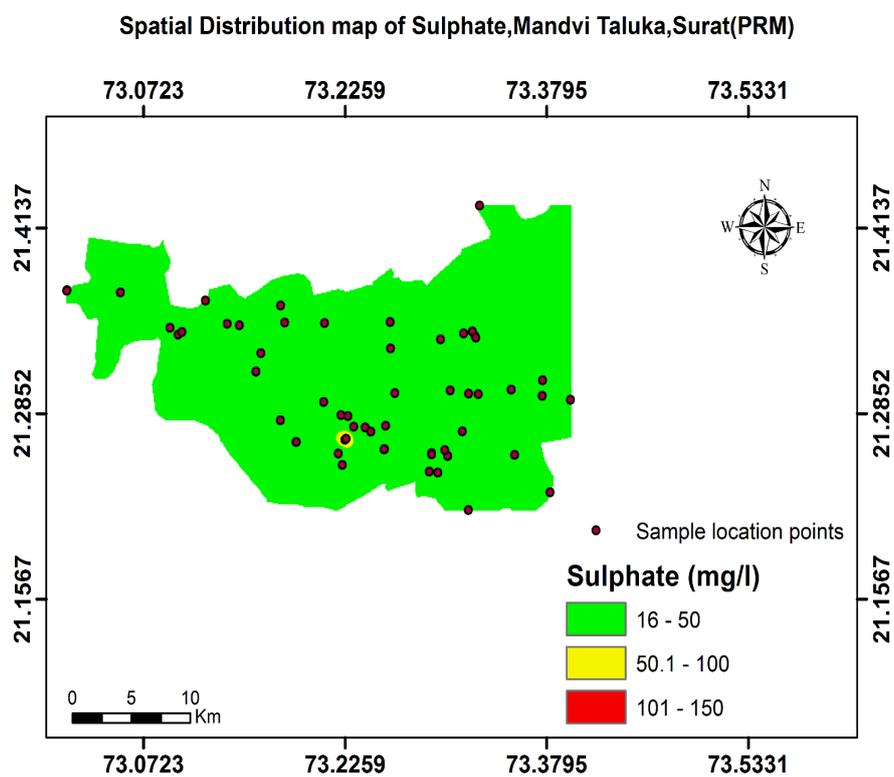
**Figure 8.** (a) Spatial Distribution map of MgH (PRM); (b) Spatial Distribution map of MgH (POM).

EC value ranges from 204 to 3971  $\mu\text{S}/\text{cm}$  which shows an increasing trend along the groundwater flow direction during POM with respect to PRM (**Figure 4(a)**)



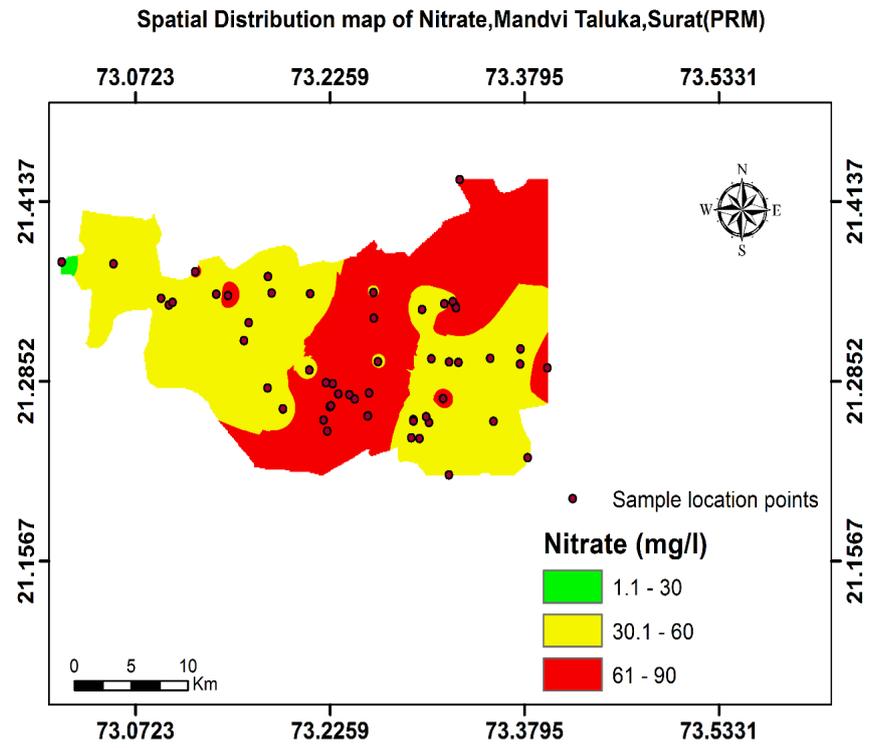
**Figure 9.** (a) Spatial Distribution map of bicarbonates (PRM); (b) Spatial Distribution map of bicarbonates (POM).

& **Figure 4(b)**). Agricultural runoff or sewage leak contains high salt content which is indicated by high EC due to the additional chloride, phosphate and nitrate ions in addition to rainfall effect and thus leads to the formation of saline soil [27]. And excess salinity reduces the osmotic activity of plants and thus

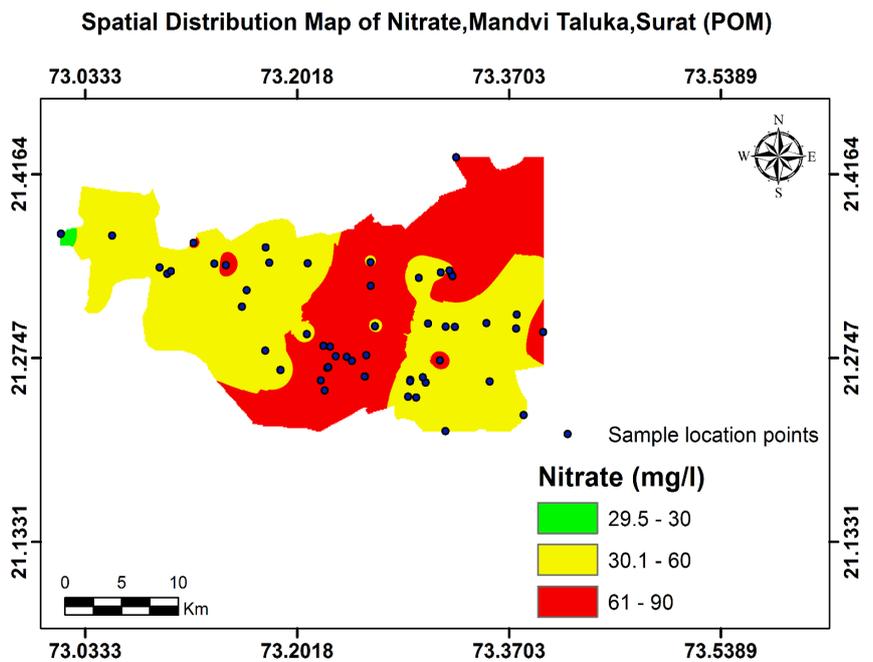


**Figure 10.** (a) Spatial Distribution map of Sulphate (PRM); (b) Spatial Distribution map of Sulphate (POM).

interferes with the absorption of water and nutrients from the soil [28]. The spatial distribution map of EC shows slight variations during POM with respect to PRM due to the effect of rainfall.



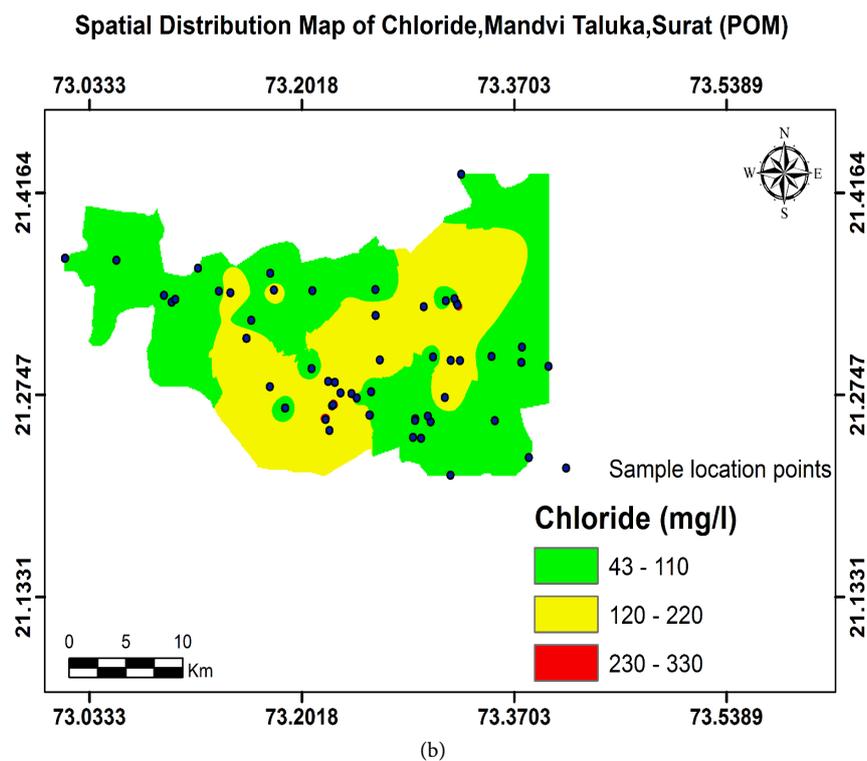
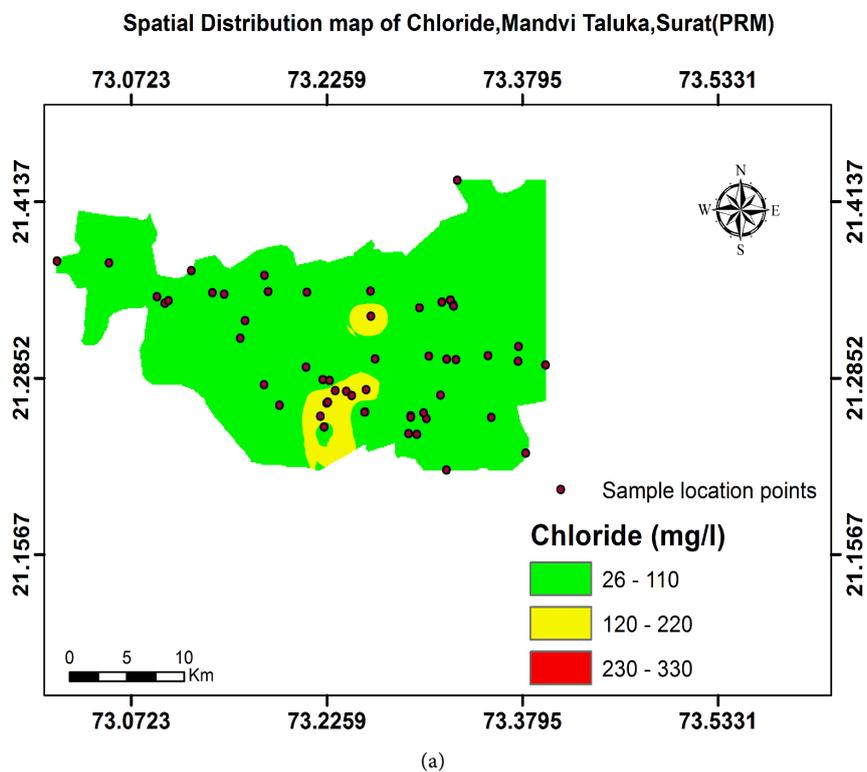
(a)



(b)

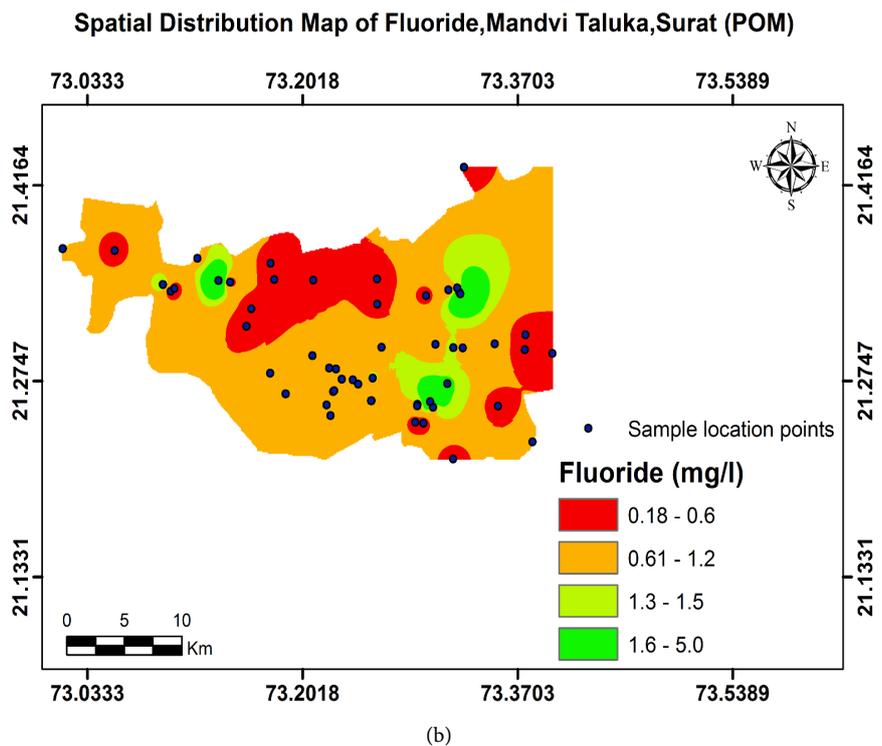
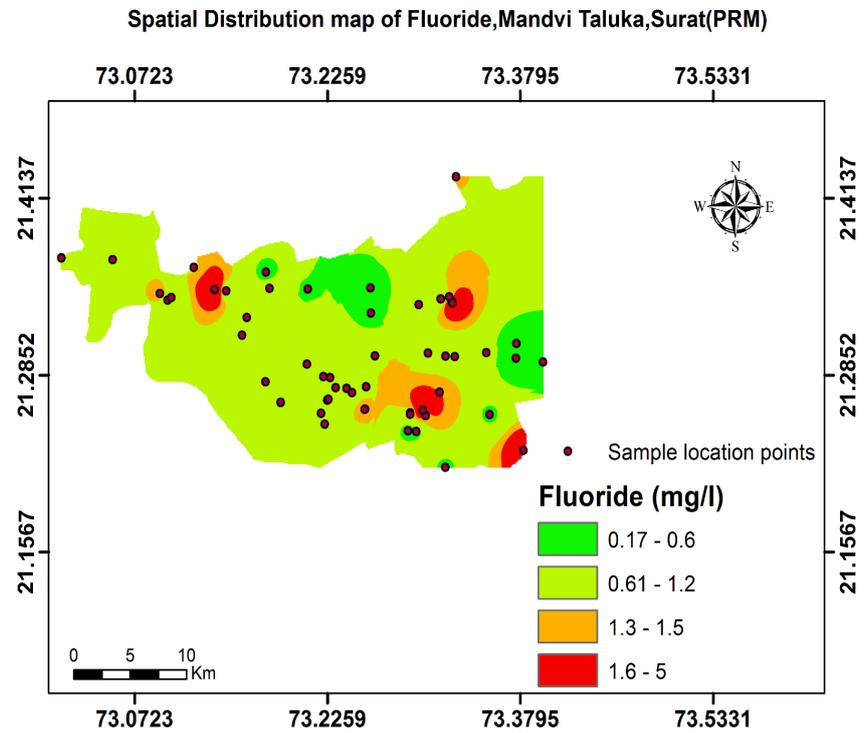
**Figure 11.** (a) Spatial Distribution map of Nitrate (PRM); (b) Spatial Distribution map of Nitrate (POM).

The Total Dissolved Solids (TDS), which indicates concentration of TDS in sample water, is between 192 to 3500 mg/l (**Figure 5(a)** & **Figure 5(b)**). Maximum number of groundwater samples from the study area exceeds the desirable



**Figure 12.** (a) Spatial Distribution map of Chloride (PRM); (b) Spatial Distribution map of Chloride (POM).

permissible limit of TDS according to Indian Standard which is caused due to the consecutive action of weathering and dilution processes or may be due to the



**Figure 13.** (a) Spatial Distribution map of Fluoride (PRM); (b) Spatial Distribution map of Fluoride (POM).

influence of anthropogenic sources, such as domestic sewage, septic tanks, and agricultural activities. To ascertain the suitability of groundwater for any purpose,

it is displayed spatially that some parts of north western, the eastern portion of the study area are exceeding the permissible limit and thus not safe for drinking and irrigation purposes. Moreover, the spatial distribution map of TDS shows increasing trend over the study area during POM as compared to the PRM period. Higher value of TDS is observed towards the NW and SE part of the study area.

The Total Hardness (TH) value ranges from 109.2 to 991.6 mg/l which signifies variation is due to the effect of weathering and erosion of soils which is acting for the period of time (**Figure 6(a)** & **Figure 6(b)**). According to Durfor and Becker classification of water types based on total hardness, 91.2% of the samples out of 57 samples are under very hard categories [29]. Ion exchange along with slow movement of groundwater during weathering results in precipitation of carbonates and thus results in high  $F^-$  associated with  $Na^+$  and low  $Ca^{2+}$  concentration [30]. The spatial distribution map of TH shows In the SE region of Mandvi Taluka, Surat, the concentration of TH is reduced during POM whereas, in the Northern side, the concentration of TH is increased during POM which is due to the presence of geological formations like basalt dykes, dolerites etc. The remaining portion of study area shows little variations between PRM and POM which is due to the influence of rainfall.

The concentration of  $Ca^{2+}$  is between 28 mg/l to 190.0 mg/l, whereas the concentration of  $Mg^{2+}$  ranges from 2.4 mg/l to 138.6 mg/l respectively. Calcium also participates in cation exchange equilibriums at aluminosilicate and other mineral surfaces. In some locations  $Mg^{2+} > Ca^{2+}$ , this may be due to the influence of sea water and also suggests that study area is having a meteoric origin in groundwater [31] [32]. Calcium and magnesium are the major constituents responsible for hardness in water and their presence is the result of the dissolution of carbonate minerals such as calcite and dolomite.

The spatial distribution map of calcium hardness (**Figure 7(a)** & **Figure 7(b)**), during PRM, shows a higher concentration of calcium towards the south western part of the study area as compared to the POM period. During POM, towards NE part of the study area in addition to NW region is showing higher concentration of calcium which is due to the dissolution of minerals towards the lower gradient of the study area. Whereas, the spatial distribution map of magnesium hardness (**Figure 8(a)** & **Figure 8(b)**) for POM shows higher concentration towards the SE part of the study area as compared to the PRM and also, there is an increase in the concentration of magnesium during POM with respect to PRM. This is due to the dissolution of ions from the geological formations such as laterite towards the lower surface elevation. Higher concentration of calcium is seen towards the NW, NE and southern part of the study area during POM as compared to PRM. This is due to the presence of geological formations such as dolerites and basalt dykes.

The major source of alkalinity includes dissolved carbon dioxide species, bicarbonates, and carbonates. Carbon dioxide species are important contributors in reactions that control the pH of natural waters. The concentration of Total

Alkalinity ranges from 160 to 706.6 mg/l, which is being controlled by bicarbonates ions. Carbon dioxide is introduced through atmospheric and biological processes contribute to the carbonate alkalinity. The action of CO<sub>2</sub> upon the alkaline material of soil and geology in the study area results in high bicarbonates in the groundwater [33]. Though, Bicarbonate is the most extensive anion, and ionic species found in groundwater, plays a most significant role in electrical conductivity. It is strongly related to many other major ions but especially more with calcium cation. However, distribution of carbonate rocks and climate is studied by the distribution pattern which helps to demonstrate climate zone. Thus, for the present study almost all the samples are bicarbonates in nature and also exceeding the desirable limit of BIS. It varies from 195.2 mg/l to 800.3 mg/l. The spatial distribution map of bicarbonate shows that in the NW region of the study area (**Figure 9(a)** & **Figure 9(b)**), the distribution of color is more during POM which shows a higher concentration of bicarbonates. This is due to the presence of geological formations like basalt, laterite etc. in the study area. The remaining portion of study area shows little variations between PRM and POM which is due to the influence of precipitation.

Sulphate is generally found in air, soil and water. Large amount of sulfur is released due to the combustion of fossil fuels. These reduced forms of sulfur in atmosphere are oxidized to sulphate in presence of oxygen and gets deposited with precipitation or deposit in dry form. Moreover, it is mobile in groundwater because it occurs as a dissolved ion. In addition to this, gypsum and sodium sulphate minerals are an important source in many aquifers containing high amount of sulphates. For the present study concentration of sulphate ranges from 13mg/l to 136 mg/l during PRM and POM and all the samples are within the permissible recommended limits (**Figure 10(a)** & **Figure 10(b)**). The spatial distribution of higher sulphate concentration is found towards NW region of the study area which is due to the dissolution of gypsum and sodium sulphate mineral which increase (SO<sub>4</sub><sup>2-</sup>) concentration in groundwater. The concentration of sulphate (SO<sub>4</sub><sup>2-</sup>) is low in groundwater which reveals the reducing condition of groundwater. The spatial distribution map of sulphate shows a higher concentration of sulphate is found during POM towards the central NW and southern part of the study area.

The amount of nitrate–nitrogen approach or exceed due to the nitrogenous organic waste, or animal waste or due to the application of chemical fertilizers. The nitrate ion concentration varies from 1.1 to 84.2 mg/l (**Figure 11(a)** & **Figure 11(b)**). All samples are within the recommended limit during PRM while three samples exceed the recommended limit during POM. Higher concentration of nitrate is seen during POM and towards NE part of the study area which may be due to leaching of agricultural chemicals or application of fertilizers or decomposition of organic matter such as animal waste or sewage [34].

All natural waters contain chloride but low in concentrations. Chloride may originate from various sources such as dissolution of crystalline and shale rocks, clay and other related minerals. Furthermore the concentration of chloride

ranges from 24 mg/l to 330 mg/l indicating dissociation and dissolution of  $\text{Cl}^-$  from the upper layer of the soil (**Figure 12(a)** & **Figure 12(b)**). All samples are within the recommended limit during PRM while three samples exceed the recommended limit during POM. In addition anthropogenic processes can locally affect chloride concentrations in ground water which include contamination from sewage or due to the influences of irrigation-return flows or application of chemical fertilizers under intensive irrigation in the study area [35] [36]. The spatial distribution map of chloride for POM illustrates that chloride is distributed all over the study area whereas, in POM period it is more towards southern and NE part of the study area.

Depending upon the prescribed range of  $\text{F}^-$  concentration given for the drinking water as per BIS-10500 the study area is categorized into three categories: less than 0.60 mg/l as low  $\text{F}^-$  category; between 0.60 - 1.20 mg/l as moderate  $\text{F}^-$  category (optimum range) and greater than 1.2 mg/l as High  $\text{F}^-$  category [37] (**Table 2**). The spatial distribution of fluoride concentration in the PRM ground waters shows that 29.8% of the total samples fall in the northern, eastern and some southern parts of the study area having the low  $\text{F}^-$  category; 22.8% of samples are distributed as high  $\text{F}^-$  category and fall in the SE, NE and little towards NW part of the study area. While remaining 50.8% of the samples fall under moderate  $\text{F}^-$  category which covers maximum area of the study area and having  $\text{F}^-$  concentration in the optimal range (**Figure 13(a)**).

During POM, 33.3% of all the samples fall in moderate  $\text{F}^-$  category *i.e.* optimum range. Whereas, 45.6% of the total groundwater samples are categorized under low- $\text{F}^-$  category and falls in the SE and NW region of the study area. The

**Table 2.** Groundwater quality with reference to Fluoride parameter in Mandvi Taluka, Surat.

Chemical Parameter	$\text{F}^-$ range (mg/l)					
	<0.6	0.6 - 1.2	>1.2	<0.6	0.6 - 1.2	>1.2
	Pre-monsoon			Post-monsoon		
pH	7.15	7.16	7.29	7.67	7.69	7.62
EC	864.11	960.18	957.12	855.59	1009.54	1003.01
TA	258.94	353.47	419	291.96	374.21	395.08
TH	316.93	324.88	272.78	349.32	294.17	276.08
$\text{Ca}^{2+}$	78.29	67.76	59.29	83.85	70.59	53.07
$\text{Mg}^{2+}$	29.42	60.08	53.29	59.58	47	52.77
$\text{F}^-$	0.38	0.91	1.98	0.34	0.92	2.12
TDS	650.94	706.59	718.15	879.12	747.42	718.83
$\text{HCO}_3^-$	315.91	431.23	511.18	352.26	452.7	511.4
$\text{SO}_4^{2-}$	28.24	31.71	37.69	43	43.79	44.67
$\text{NO}_3^-$	10.84	11.48	12.23	33.84	32.83	30.43
$\text{Cl}^-$	52.59	67.97	72.77	88.12	114.06	137.75

All the anion and cation values are shown in mg/l, except Temperature in  $^{\circ}\text{C}$  & EC in  $\mu\text{S}/\text{cm}$  at  $25^{\circ}\text{C}$ .

remaining water samples (21.1%), are classified as high  $F^-$  category, and are towards the NE, NW and southern parts of the study area. It was observed that Fluoride ( $F^-$ ) concentration was higher during POM which may be due to the dissolution and precipitation of  $F^-$  bearing minerals along with the adsorption/desorption from metal (hydro) oxides and clay minerals which are found under alkaline conditions and that goes weathering chemical process which leads to higher concentration of Fluoride (**Figure 13(b)**).

Usually, precipitation of salts, together with fluoride salts, remains in the upper layer of soil is caused due to the high rate of evapotranspiration and this act as source for easily dissolvable fluorine after monsoon. While during POM, an adequate addition of Fluoride with an increase in TDS results in high concentrations of salts due to the leaching of infiltrating waters from the soils [38] [39].

Moreover, the increase in contact time increases the ion-exchange between  $OH^-$  in water to  $F^-$  in the mineral and these results in enhancing the concentration of  $F^-$  in ground waters. Further, higher values of TDS also increase the dissolution of  $CaF_2$  in the ground water [40]. In addition, there was influence of anthropogenic sources, such as domestic sewage, septic tanks, and agricultural activities which affect the concentration of Fluoride.

Also, as shown in **Figure 1**, the rocks present in study area such as basalt, rhyolites, dolerite/basalt dyke, laterite, argillaceous limestone, sandstone and clay were major source of fluorite [41] [42]. Generally, in fluoride bearing minerals present in rocks and clayey soil an ion-exchange process replaces the  $F^-$  by  $OH^-$ . Thus, the presence of  $F^-$  in the ground water of study area has been characterized to the host rocks, which can also justified with a positive relationship established between the  $F^-$  content in the bulk rocks and in the associated ground water [43] [44] [45] [46].

Moreover, intensive and long-term irrigation with heavy application of fertilizers in the district could be another factor that causes weathering and leaching through circulating water from the weathered products which dissolves and leaches the minerals, including fluorine [43] [44] [45] [46]. Moreover, due to the wet and dry conditions in the semi-arid region of study area also enhances the fluoride dissolution through minerals present in soil and rocks. Thus, the increased contribution of fluoride was observed.

#### 4. Conclusion

From the detailed analysis and study, it can be said that by the action of carbon dioxide in water on carbonate rocks such as Basalt, Rhyolites, Dolerite/Basalt dyke, Laterite, Argillaceous limestone and clay containing nummulites and clay, friable sandstone, pebbly sandstone, conglomerate etc., high amount of bicarbonates ( $HCO_3^-$ ) are produced and thus forming an alkaline environment. In addition this, chemical weathering under semiarid conditions with high TDS, low total hardness in the rocks and soils with hydro-geochemical processes like dissociation, ion-exchange, dissolution, and some anthropogenic inputs like the

heavy use of fertilizers, domestic sewage, leakage from septic tank and animal waste which affect the concentration of fluoride and contributing fluoride to the ground water. Thus, due to the dissolution and precipitation of F<sup>-</sup> bearing minerals along with the adsorption/desorption from metal (hydro) oxides and clay minerals which are found under alkaline conditions and that goes weathering chemical process which leads to higher concentration of Fluoride.

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