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Salinization and Deterioration of Groundwater Quality by Nitrate and Fluoride in the Chittur Block, Palakkad, Kerala

E. Shaji,[a*], Gómez-Alday, J.J.[b], Hussein, S.[c], Deepu, T. R.[a] and Anilkumar, Y.[a]

[a] Department of Geology, University of Kerala, Kariavattom Campus, Trivandrum - 695 581, India
[b] Hydrogeology Group, Institute for Regional Development (IRD), University of Castilla-La Mancha (UCLM), Albacete, Spain
[c] Department of Geology, Faculty of Science, United Arab Emirates University (UAEU), Al Ain, United Arab Emirates
E-mail: *shajigeology@gmail.com*

ABSTRACT

Chittur block represents a mid-land region of Palakkad district, Kerala and the block differs from the rest of the blocks in its climate and availability of groundwater. About 75% of the people depend on agriculture for their livelihood. Results showed that groundwater salinity levels (up to 1,963 mg/L TDS),fluoride (up to 6.3 mg/L) and nitrate (up to 141 mg/L) contents have increased significantly in tandem with the increase in groundwater abstraction. Before human intervention the chemical weathering of gneisses and granites was the main process impinging on the chemical signature of groundwater. The initial chemical equilibrium conditions change with increasing groundwater withdrawal rates and fertilizer input, in a milieu of lower natural groundwater recharge. The appearance of higher levels of bicarbonate, linked to denitrification processes, and the decrease in calcium, due to calcite precipitation, can lead to increased content of sodium and fluoride in groundwater. In this scenario the use of groundwater resources for human consumption and agriculture represents a public health risk if water management actions do not change the trend in water use in the near future. The potential loss of fertile soil by groundwater salinization must also be considered when planning sustainable policies in a region with over dependence on groundwater resources.

INTRODUCTION

Groundwater quality preservation is one of the major concerns worldwide. The Government of India affirms that groundwater has become one of the important sources of water for meeting the requirements of various economic sectors since the last few decades. Agricultural development, industrialization and urbanization have lead to the overexploitation and contamination of groundwater resources in some hydrogeological systems in India. These facts result in adverse environmental impacts and threaten the long-term sustainability of water resources (CGWB, 2010). Groundwater quality depends on water-rock interactions, in which geology and weathering can play an important role, as also anthropogenic activities and climate. Changes in land use are one of the most influential factors in groundwater pollution (Benson et al. 2006; De Andrade et al. 2008; Jiang et al. 2008; Jalali 2009; Martín-Queller et al. 2010).

On a global scale, Flowers (1999) pointed out that salinity has already affected approximately 50% of all irrigated land. Martinez-Beltran and Manzur (2005) calculated the total global soils affected by salt at 8.31 Mkm^2. Salinity can cause yield reduction in agriculture, by driving metabolic dysfunctions in plants due to osmotic stress and the disruption of ion homeostasis (Hasegawa et al. 2000). Increasing soil salinization is also occurring in India (Wichelns, 1999). Salinity always exists in ground water but in variable amounts. It is mostly influenced by aquifer material, solubility of minerals, duration of contact and factors such as the permeability of soil, drainage facilities, quantity of rainfall and above all, the climate of the area.

Around 200 million people in 25 nations are in great risk of fluoride (F^-)-induced diseases (Ayoob and Gupta 2006). In India about 60-65 million people use F^-contaminated groundwater for drinking. China is one of the the worst affected countries (Jadhav et al 2015). Many states from India are afflicted with fluorosis (Panda et al. 2012 and references therein). Fluoride in small concentrations (<1.0 mg/L) has been tested to be beneficial in reducing the incidence of dental carries by formation of dental enamel (Bell and Kudwing 1970). The use of fluoride-contaminated drinking water is a well-known risk factor for public health (Mahramanhioglu et al. 2002; Jadhav et al. 2015). Due to the strong electronegativity of F^-, it is attracted by Ca^{2+} in bones and teeth (Susheela et al. 1993). Fluoride contents higher than 1.5 mg/L are not suitable for drinking purposes. Such concentrations in groundwater have resulted in staining of tooth enamel. Fluoride concentrations ranging between 5.0 and 10.0 mg/L may lead to bone deformation. Fluoride content in groundwater in India varies considerably (Handa 1975, Rafique et al. 2009, Reddy et al. 2010, Singh and Mukherjee 2015). Similar results were found while studying the occurrence of F^- in the Palamu district (Jharkhand, India) up to 4.2 mg/L (Raju et al., 2012). High F^- groundwater (up to 5.75 mg/L) has been reported from both phreatic and deeper aquifers in the eastern part of Palakkad district (Shaji et al, 2007, Deepu and Shaji 2011) and in sedimentary aquifers of Alleppey (Raj and Shaji, 2017).

Groundwater deterioration by NO_3^- degrades the groundwater quality and impacts negatively on ecosystems. Elevated NO_3^- contents in drinking water is a health concern since the endogenous reduction of NO_3^- to NO_2^-, and the nitrosation of nitrites can form N-nitroso compounds which have been described as cancer precursors (Gulis et al., 2002; De Roos et al., 2003; Ward et al., 2005; Yang et al, 2007). The long-lasting impact of NO_3^- contamination is more important in rural areas of the developing world where groundwater constitutes the main source of potable water. Nitrate contamination in some agricultural regions of India are as high as 684 mg/L (Anantapur district; Suthar et al. 2009 and references therein). Recently, Brindha et al. (2012, 2013) found that the high NO_3^- concentration (up to 879.65 mg/L) in groundwater in Nalgonda district (Andhra Pradesh) is due to deficient sanitation services and leaching from animal waste.

This work investigates the mechanisms and geochemistry of salinization with special emphasis on its relationship with the fate of fluoride and nitrate in order to identify plausible geochemical reactions under the current exploitation regime.

In Kerala, over dependence on groundwater for domestic, irrigation and industrial purposes has led to the lowering of water table and water scarcity (CGWB, 2007).

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STUDY AREA

The study area (Chittur) lies in the Palakkad (Palghat) district, Kerala (Figure 1A and B). The area lies between 10° 37' and 10°48' N latitudes and 76°41' and 76°54' E longitudes. The block, 261 km^2 in extent, represents a mid-land region (Figure 1B). There are six panchayaths, 20 villages and 37 micro watersheds in the block. This is one of the agrarian blocks of the district. The main profession of the populace is farming. The total population of the block as per 2011 census is 190,931 with a decadal growth of 5.9%. Irrigation is mainly rainfed, groundwater based and through canals. This block differs from the rest of blocks in the Palakkad district in its climate because of a unique gap in the Western Ghats called 'Palghat gap'. This gap influences the rainfall, temperature and wind pattern of the region. It is mostly a rain shadow region and the block receives an annual average rainfall of 1,413 mm against the district average of 2,348 mm. The annual potential evapotranspiration (PET) for Palakkad is 1662.7 mm for the period 1960-2010. The highest PET value is recorded during March amounting to 192.0 mm and the lowest of 100.3 mm (July). PET is less than rainfall during May to October (CGWB, 2009). Total numbers of rainy days are 108. The mean maximum temperature is 34^{0}C with a minimum of 23.4^{0}C. Relative humidity is high in morning hours (79%) and low in the evenings(63%).

During last two decades many a times Chittur was declared as drought affected as it showed a significant and progressive decline of both premonsoon and postmonsoon water table levels. According to the categorization for groundwater development (CGWB, 2007, 2015), the block has been declared over exploited.

Inland salinity is observed very close to the study area in areas like Nedupeni, Koduvayoor, Kozhinjampara and Gopalapuram and it is also noticed from the western part of the Kadumthuruthi (Yakkara) and Kuduvayoor areas. About 1 km^2 area is affected in both areas (Shaji, 2009).

A considerable change in the land use and cropping pattern has occurred in the Chittur block for the last five years (CGWB 2007). Due to low income from paddy and coconut, farmers are changing the cropping pattern to more profitable crops like sugarcane, vegetables and flower cultivation. The major crops cultivated in the zone are paddy, coconut, arecanut, banana, tapioca and vegetables. As per estimates, paddy is the most important crop having the largest area under cultivation during the period 2007-2008 (113.63 km^2). Parts of Chittur block are potential rice growing areas and are well irrigated by the Chittur-Thathamangalam irrigation project.

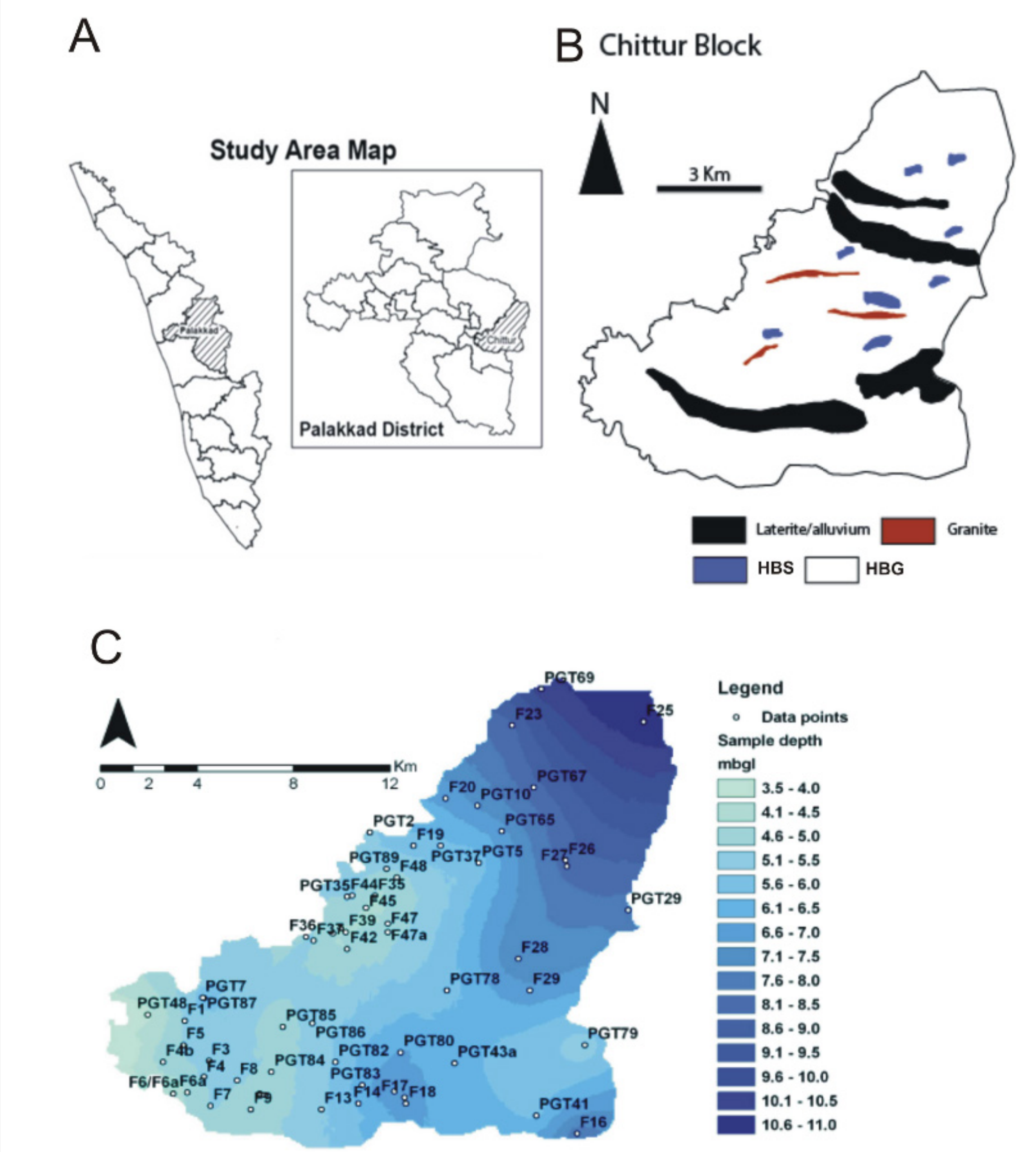

Fig.1. (A) Location of study area, **(B)** geologic map of the Chittur Block and (C) groundwater level map for pre-monsoon 2011 period with location of data points mbgl: meters below ground level. HBG: Hornblende Biotite Gneiss, HBS: Hornblende Biotite Schist.

Geomorphologically, the area can be broadly classified as mid land. The landform units of the area are valley fill, pediment and denudational hill. The valley fill occupies an area of 112 km^2, denudation hill 21 km^2 and the pediment 133 km^2. The pediment predominates (50%) among different landform categories. The area comes under Chittoorpuzha sub-basin of Bhratapuzha river basins. The drainage pattern is dendritic with third order streams joining Chittoorpuzha. There are three types of soil in the block: laterite, black cotton and alluvial. Laterite soil is the most predominant soil type in the midland and gap areas. They are products of weathering of hornblende biotite gneisses and granites. Black soil is another common type of soil which is used for the cultivation of cotton. The pH is about 7.0, and has high clay and medium contents of organic matter (Source: RSVY Document of GOK and Vikasanarekha of LSGs and KrishiBhavan data collected from Kerala Agriculture University (personal communication)). Alluvial soil appears along the banks of Chitturpuzha and other tributaries in varying thickness. The main surface water sources of the area are tanks/ponds, Moolathara reservoir and Kambalathara lake. There are numerous tanks/ponds and drainage channels in the area. Moolathara irrigation project and canals of Chittur Puzha project provide water for irrigation in the study area. 75% of the population depends on groundwater resources for their irrigations needs and 25% from the irrigation schemes (major and minor).

METHODOLOGY

A base map has been prepared for the study area using Survey of India toposheets 58B/10 and 14. Domestic wells have been established in the study area for water level monitoring and sample collection (Fig.1C). The well locations and other details are transferred to the geographic information systems (GIS)-based map. Depth to water level, total depth, diameter, well section and geology were recorded. Water level data has been analyzed and water level contour maps have been prepared using ArcGIS software. GIS maps were projected in WGS-1984, UTM zone 43N, using transverse mercator projection.

In the present study a total of 61groundwater samples (50 dug well water samples, 11 bore well water); were collected from hard rock aquifers (April, 2011). Chemical analyses were carried out in the chemical lab of the Department of Geology, University of Kerala following the official standard methods for water analysis (APHA-AWWA-WPCF 1998). Fluoride, $SO_4^{2''}$, NO_3^-, and $Cl^{''}$ were measured using ion chromatography at Indian Institute of Technology (Chennai), Na^+ and K^+ were determined by atomic emission spectroscopy, and $HCO_3^{''}$, Ca^{2+}, and Mg^{2+} by complexometry using the volumetric method. Total dissolved solids (TDS) and pH were measured in the field by means of portable electrodes.

For geostatistical purposes the kriging method was used for mapping groundwater levels and ion concentrations. Kriging assumes that the data comes from a stationary stochastic process and some methods assume normally-distributed data. This method of interpolation was used to obtain the spatial distribution of the main chemical parameters of the groundwater quality since the spatial estimation procedure provides the best linear unbiased estimator with the minimum variance. To explain the relationship of groundwater chemistry and water level evolution, the average ion contents for the study period were calculated and compared to average depth to sample data. The water level evolution has been addressed by considering that the depth of the water sample represents the water level.

RESULTS

Hydrogeology

In the study area groundwater occurs in all the geological formations from Archaean crystalline to Recent alluvium. The major rock units are hornblende biotite gneiss, hornblende biotite schists and granite (Fig.1B, modified after GSI,1995). Groundwater is in semiconfined to confined condition in the deep fractured aquifer. Fractured crystalline rocks show more than two sets of fractures (CGWB 2010). The major fracture in the E-W direction is highly yielding. Vertical to sub-vertical narrow linear zones of limited width occur at Velanthavalam, Chittur and Kozhinjampara. Horizontal to sub-horizontal zones of varying thickness are encountered at various depths alternating with massive blocks as in Kozhipara and Kozhinjampara, Eruthenpathy locations.

Groundwater occurs in phreatic condition in the laterite, alluvium and weathered crystalline rocks. Alluvium is encountered along the banks of rivers and valley fills. The thickness of laterisation and weathering varies from 2.0 to 15.5 mbgl. The thickness (2 to 15 m) as well as the width (2 m to 1 km) of the alluvium increases towards the west and around Chittur. The depth of the weathered strata controls the groundwater occurrence in the dug wells and increases towards the western part of the area where dug wells have higher groundwater potential compared to the rest. Several rural water supply schemes have tapped this zone. The general depth of water level varies from 4.0 to 11.5 mbgl and the depth of wells ranges from 4.4 to 15.0mbgl. The yield of the wells tapping alluvium ranges from 5,000 to 50,000 l/d. In the laterite/alluvial province groundwater occurs under phreatic conditions which are minimal in areal extent. The depth of wells ranges from 5 to 12 mbgl. The diameter of the well ranges from 2 to 5 m. The deepest water level is recorded from Ozhalapathy and Vannamada areas. The yield of dugwells ranges from 5 m^3/hr to 10 m^3/hr. During post monsoon period in 2011 the depth to water levelranged from 1.81 mbgl to 11.93 mbgl. Potentiometric surface indicates that groundwater level decreased towards the NE area of the Chittur block (Figure 1C). In the central and SW area, the water level drop is less pronounced. As a result the potentiometric surface showed a curved morphology with lower water levels coinciding with the presence of cone of depressions driven by intensive groundwater withdrawal. The difference in groundwater levels between the central and NE areas can be as high as 7 m, which implies a drop trend of about 0.6 m/km.

Hydrochemistry

Basic statistics of physico-chemical parameters are given in Table 1. The major cation and anion concentrations of the groundwater were plotted on a Piper diagram (Fig.2). In the Piper plot sampling points were distributed along a mixing line: the groundwater of the NE of Chittur Block was characterized by Na-Cl hydrofacies; groundwater in the central areas was represented by Mg-Ca-Na-HCO_3 hydrofacies. Major cations and anions were arranged according to their decreasing concentrations as anions: $HCO_3^- > Cl^- > SO_4^{2-}$, although the difference between HCO_3^- and Cl^- is depreciable, cations: $Na^+ > Mg^{+2} > Ca^{+2} > K^+$.

Groundwater pH values vary between 6.5 to 8.1 in the sampling period (March to May 2011). Total dissolved solids ranged between 184 mg/L (300 µS/cm) and 1,963 mg/L (3,200 µS/cm). Alkalinity (as HCO_3^-) ranged from 15 mg/L to 305 mg/L. Sulphate concentration in groundwater ranged from 3.2 mg/L to 249.1mg/L. Chloride contents ranged from 24.9 mg/L to 553.8 mg/L. The ranges for the other cations are: Na^+: 13mg/L to 134mg/L, Ca^{2+}: 25.1 mg/L and 105.2 mg/L, Mg^{2+}:14.5 to 123.9 mg/L, K^+: 1 mg/L to 43 mg/L. Except in one sample corresponding with the data point F19 in which F^- is 6.3 mg/L, the concentration of this anion ranged from 0.05 mg/L (detection limit) to 2.3 mg/L (Mean value: 0.5 mg/L; n = 60). Nitrate concentrations ranged from 1.4 mg/L and 141.1 mg/L. The dug wells show F^- ranging from 1.00 to 5.75 mg/L (Kopanur area). The bore wells also show high concentrations of fluoride F^-, between 0.30 and 3.12 mg/L (bore well at Chinnamoolathara area). The water supply bore well of Eruthanpathy showed 1.76 mg/L of F^-.

Table 1 Summary for the basic statistics of physico-chemical parameters for the study period in the Chittur block. Minimum: min, Maximum: Max, Average: Av, n: number of samples, EC: Electrical conductivity (µS/cm). Concentration of ions and total hardness and total alkaliniby in mg/L

	Min.	Max.	Avg.	n
pH	6.50	8.12	7.20	61
EC	300	3200	985	61
TDS	184	1963	604	61
Total Hardness	125	565	228	60
Total Alkalinity	20.0	355.0	100.9	60
K^{+}	1.0	43.0	3.3	60
Na^{+}	13.0	134.0	43.6	61
Ca^{2+}	10.0	46.1	23.7	61
Mg^{2+}	14.5	123.9	40.6	61
SO$_4^{2-}$	3.2	249.1	36.3	61
Cl^{-}	24.9	553.8	98.4	61
F^{-}	0.05	6.30	0.62	61
NO$_3^{-}$	1.4	141.1	25.3	61

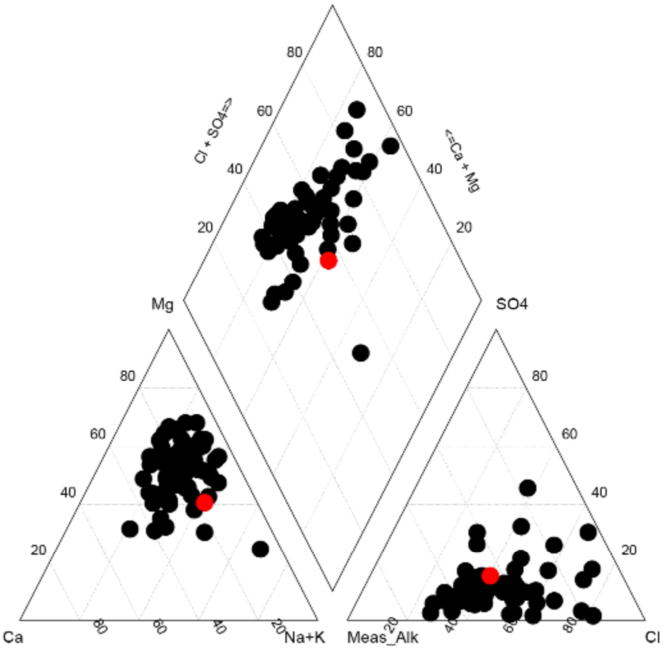

Fig.2. Piper (1944) diagram for the study period.

DISCUSSION

Groundwater Quality Status for Drinking and Irrigation Purposes

According to Bureau of Indian Standards (BIS), about 81.9% of the analysed samples had values above the threshold limit of 500 mg/L TDS (extended to a TDS of 2,000 mg/L in case no other source is available (BIS 2009)). Values of TDS in excess of 2,000 mg/L were observed in 6.5% of the samples. Coupled with the appearance of salinity, an increase in total hardness was also found (elevated SO$_4^{2-}$, Cl^{-}, Ca^{2+}, Mg^{2+}, Na^{+},F^{-}, and NO$_3^{-}$concentrations). Thus, total hardness (as CaCO$_3$) concentrations ranged from 125 to 565 mg/L. The 16.6% of the water samples had values above the threshold limit of 200 mg/L but none of them reached the limit of 600 mg/L (the limit stated when no alternative sources of water can be found). About 3.3% of the samples had values above the threshold limit of 200 mg/L of SO$_4^{2-}$ recommended by BIS (2009) (extended to 400 mg/L in case of no alternative sources are available). Up to 6.5% of the collected samples had values above the threshold limit of 250 mg/L Cl^{-} (extended to 1000 mg/L in case no alternative sources are available). BIS has recommended a limit of 55 mg/L of Ca^{2+} in drinking water (extended to 200 mg/L in the absence of alternative water sources). About 65.6% of the samples had values above the threshold limit of 50 mg/L, but none of the analysed samples reach the uppermost limit of 200 mg/L. All of the analysed samples surpass the limit stated in 30 mg/L for Mg^{2+} contents in groundwater by BIS. BIS recommended a maximum concentration level of 1.0 mg/L of F^{-} as desirable concentration in drinking water; this parametric value can be extended to 1.5 mg/L in case no alternative sources are available. Fluoride contents in groundwater higher than 1.5 mg/L have been detected in 4.9% of the analysed samples. Thirteen percent of the samples had values higher than the threshold limit of 50 mg/L NO$_3^{-}$ stated by BIS. These results are evidence for the deterioration of groundwater resources for human consumption in the study area. The worsening of water quality is noticeable in the NE part of the block.

Evaluation of groundwater salinization is essential in the assessment of water quality for irrigation purposes, since salinization may lead to the loss of soil productivity in the future. For assessing the irrigation water quality the total salt concentration as measured by EC (or TDS) and the relative proportions of sodium (Na^{+}), magnesium (Mg^{2+}), and calcium (Ca^{2+}) in groundwater is measured. Results indicated that TDS concentration in the Chittur Block ranged from 184mg/L to 1,963 mg/L. According to the groundwater classification based on TDS contents (Freeze and Cherry 1979), the groundwater in the area ranged between freshwater (0-1,000 mg/L) and brackish water (1,000-10,000 mg/L). Interpolated TDS values increased towards the NE and SW areas of the Chittur Block (Fig.3A). The fraction of exchangeable Na^{+} is a function of the ratio of Na^{+} over the square root of Ca^{2+} and Mg^{2+} concentrations as a measure of the sodium absorption ratio (SAR). Sodium absorption ratio values, which ranged from 0.4 to 2.5, showed a trend towards higher values in the NE and SW area of the Chittur block on a similar pattern to the TDS spatial distribution (Fig.3B).The plot of the samples in a Wilcox diagram, which relates TDS values and SAR index, indicated a hydrochemical trend towards more deteriorated groundwater in the NE Chitturblock (Fig.4). The plotted samples indicate that the Na^{+} hazard was low (S1) except for one sample (SW13) whilst the salinity hazard ranged from medium (C2) to very high (C4). The low sodium hazard can be indicative of the cation exchange capacity of the media to maintain low values of dissolved Na^{+} in groundwater.

Groundwater Salinization Processes

Total dissolved solids and SAR values can be visually correlated to the sample depth suggesting that the hydrogeochemical evolution is associated with the exploitation regime of groundwater (Fig.1C, 3 A, B). The spatial coincidence of declining groundwater levels and increasing TDS values indicate that the driving force is the regime of groundwater withdrawal. Groundwater deterioration processes are more important in the NE part of the Chittur Block where groundwater abstraction is intense.

Total dissolved solid contents changed parallel to the groundwater flow, enabling inferences on the deterioration processes in groundwater. The difference in TDS values can be as high as 1,500 mg/L. Thus, as a proxy figure, each meter of decline implies an augmentation of 220 mg/L in TDS contents. Salinization of groundwater is usually related to seawater intrusion and mixing with external saline waters (Vengosh, 2003). In seawater there is a predominance of Na^{+} and Cl^{-} with a molar ratio of 0.86, an excess of Cl^{-} over the alkali ions (Na^{+}+K^{+}), and Mg^{2+} greatly in excess of Ca^{2+}(Ca/Mg = 0.20–0.22; see Table 1 in Vengosh 2003). In the Chittur Block, Na/Cl molar ratio changed from 0.3 to 1.9 (only one sample gave a value of 3.2). Although the value of the determination coefficient is low (R^2 = 0.20, data not shown), the highest values matched with lower TDS concentrations, indicating a relative increase in Na^{+} in those regions of the aquifer less affected by

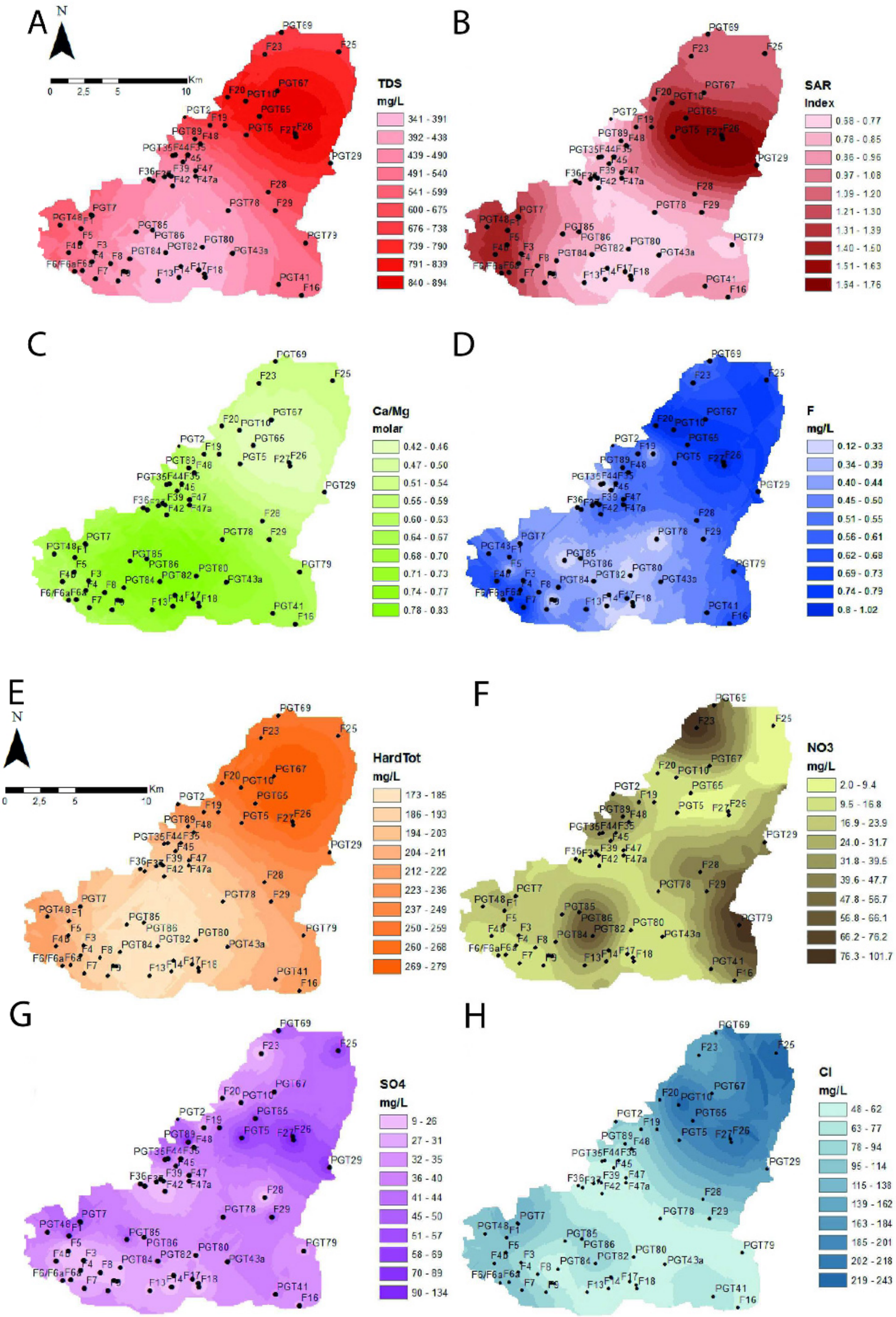

Fig.3. Interpolated maps for Total Dissolved Solids (TDS) **(A)**, Sodium Adsorption Ratio (SAR) values **(B)**, Ca/Mg molar ratio **(C)**, F^- **(D)**, total hardness **(E)**, NO_3^- **(F)**, SO_4^{2-} **(G)**, Cl^- **(H)** in the Chittur Block.

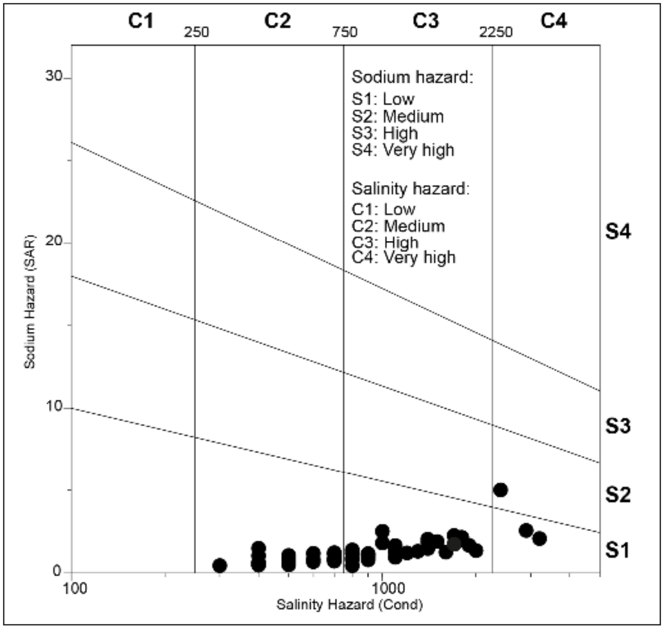

Fig.4. Wilcox type diagram of groundwater samples from the study period. Cond.: Electrical Conductivity (uS/cm).

salinization. Thus it is proved that a loss of Na^+ relative to Cl^- happens in groundwater samples with increasing TDS values, as shown in the Na^+ vs Cl^- scatter plot (Fig.5). The Ca/Mg ratio in the groundwater samples were between 0.10 and 1.42 (mean value of 0.30). The lowest values corresponded with high TDS concentrations (R^2 = 0.41), indicating a relative increase in this ratio in those regions of the aquifer less affected by salinization. An increasing trend in the concentration of $Mg^{2+}$with increasing TDS values were observed but this trend was not observed in the case of Ca^{2+}cation (Fig.6).

In many cases, the saline water can lead to $Ca/(SO_4+HCO_3) > 1$. Except for one sample in which $Ca/(SO_4+HCO_3)$ ratio was equal to 3.4, results obtained in this study showed that this ratio ranged between 0.05 and 0.6. The lower values of the ratio matched with higher TDS concentrations (R^2 = 0.31, data not shown), indicating that the loss of Ca^{2+} is balanced by the increasing concentrations in SO_4^{2-} and HCO_3^-. The molar ratio $HCO_3/(SO_4+HCO_3)$ varied from 0.18 to 0.98 (mean value: 0.84; n = 60) and it seems to decrease with increasing TDS, although the determination coefficient is not high (R^2 = 0.23, data not shown). The proportion of these anions indicated the relative dominance of two major sources of protons during water-rock interactions such as carbonic acid and sulphide oxidation reactions. The areas with lower TDS values, up to 184 mg/L, were represented by Mg-Ca-Na-HCO_3 hydrofacies which are commonly found in groundwater from igneous terrains (Gómez and Turrero, 1994). Therefore, water chemistry was initially controlled by the weathering of silicate rocks.

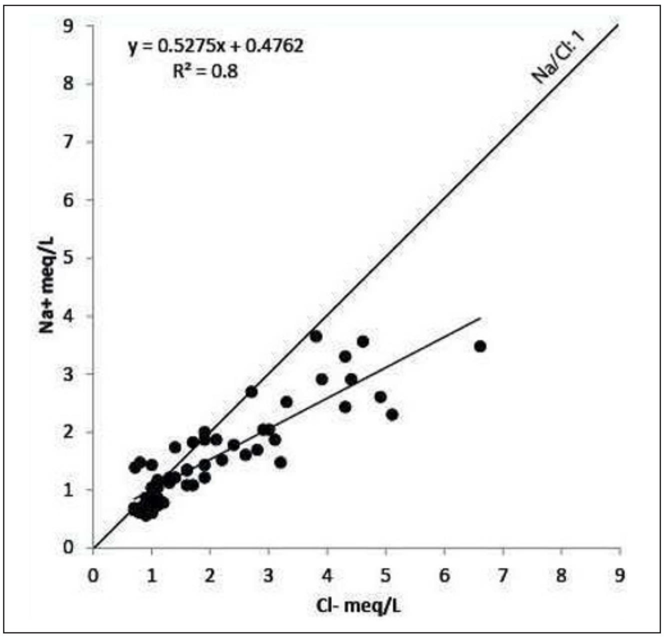

Fig.5..Sodium versus Cl^- values in groundwater samples from Chittur Block.

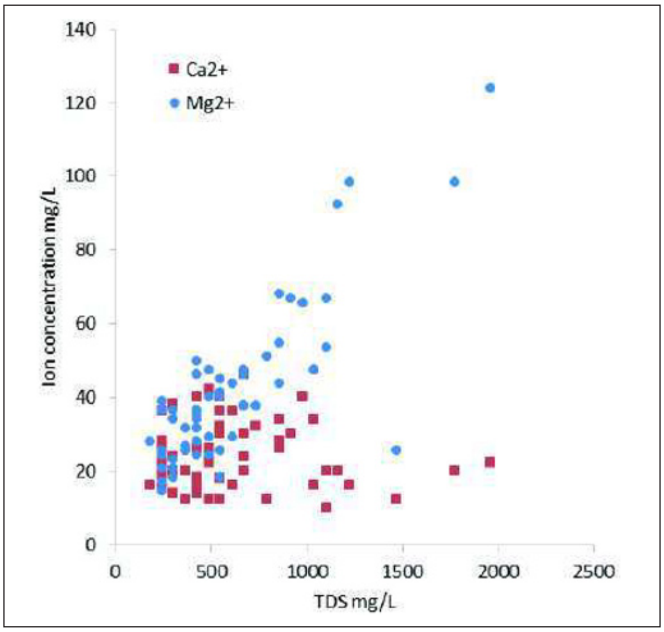

Fig.6. Evolution of the concentration of $Mg^{2+}$and Ca^{2+} concentrations with increasingly TDS values.

Salinization processes lead to changes in groundwater chemistry which could lead to misleading interpretations on solute sources. In those areas with increasing TDS contents, water chemistry changed to chloride, magnesium and sodium type, losing its primary hydrochemical signature, and acquiring ionic ratios close to those exhibited typically by seawater (i.e. Ca/Mg ratio).-The increase in the SAR index in groundwater is indicative of the relative enrichment in Na^+ and the relative loss of Ca^{2+} over Mg^{2+}. During cation exchange processes, Na^+ in the solution can be exchanged by $Ca^{2+}$and/or Mg^{2+} from clay minerals. This results in a loss of Na^+ relative to Cl^- in groundwater samples (Fig.5). Coupled with the decrease of Na^+ in solution, Ca^{2+} and Mg^{2+} increase in groundwater. Calcium and Mg^{2+} concentrations increase towards those areas with higher TDS concentrations. The highest Na/Cl ratios matched with lower interpolated Ca/Mg (Fig.3C) ratio as a consequence of the increase of Mg^{2+} in groundwater and relative loss of Ca^{2+}. The processes which can explain the increase of Na^+ in relation to Ca^{2+} and Mg^{2+} can be the precipitation of Ca^{2+} and Mg^{2+} bearing minerals. The removal of Ca^{2+} in the groundwater system is by the cation exchange and calcite precipitation processes. Precipitation of carbonate minerals (i.e. calcite) can also lead to the excess of Mg^{2+} in groundwater since dolomite is not thermodynamically favoured (Appelo and Postma, 2005).

Human activities like over pumping of groundwater can enhance salinization processes (Jones et al. 1999). In spite of the amount of precipitation (annual average rainfall of 1,413 mm), the withdrawal of groundwater is above the renewal capacity of the aquifer, This couple with elevated evapotranspiration rates can lead to the abstraction of groundwater with higher TDS concentrations. The mixing of pristine groundwater with saline waters can also explain the increase in salinity and the chemical modifications occurring along with the hydraulic gradient. The negative water balance driven groundwater abstractions and evapotranspiration processes are exacerbated by the drought events that occurred during 2002, 2008, 2009 and 2012. The vegetable cultivation is badly affected in some areas. It is noticed that the cucumber and its leafs show some discolouration due to the high concentration of sodium in the irrigated groundwater

Fluoride in Groundwater

Fluoride presence in groundwater can be related to the natural breakdown of minerals in igneous and sedimentary rocks and soils, and to the weathering and deposition of atmospheric particles (see Saxena and Ahmed, 2003, Dhiman and Keshari, 2006). Fluoride exists in the form of fluorides in a number of minerals such as cryolite (Na_3AlF_6), fluorapatite ($Ca_5(PO_4)_3F$) and fluorite (CaF_2). The crystalline rocks of the study area consist mainly on F-bearing biotite and hornblende. In the Chittur Block, the sources of F^- are identified as biotite and hornblende from the rock hornblende biotite gneiss (Jacks et al 1995, Shaji 2012).

The interpolation of F^- contents showed a trend towards higher values in the NE and SW areas (Table 1, Fig.3D) whereas the central part of the block exhibited the lowest values. The presence of other sources of Ca^{2+} and F^- in groundwater can modify the solubility of fluorite as stated by the law of mass action. During chemical weathering, the dissolution of fluoride minerals is controlled by dissolved $Ca^{2+}$and thermodynamic of the reactive processes. Considering that the F^- concentration in groundwater is controlled by the mineral fluorite according to Brown and Roberson (1977):

$$CaF_2 = Ca^{2+} + 2F^-$$
$$K_{CaF_2} = a(Ca^{2+})$$
$$a(F^-)_2 = 10^{-10.58} \text{ at } 25°C, 1 \text{ atm}$$

where K represents the solubility product constant and a are the activities, considering activities equal molalities of the ions considered.

The results obtained in this study demonstrate that the groundwater samples are subsaturated in the mineral fluorite (Fig.7). Samples plotted closer to the line which defines the $\log K_{fluorite}$ belong to data points located in the areas corresponding to high TDS concentrations, total hardness values, and low Ca/Mg ratio (Figs. 3A, B, D). Dhiman and Keshari (2006) point out that fluoride has negative relationships with calcium, whereas relationships with sodium, alkalinity and sulphate are positive in Mehsana District (Gujarat, India). Equilibrium condition of the water solution with fluorite is a straight line which imposes that groundwater with low Ca^{2+} contents would contain high F^- concentrations. Field data indicated that Ca^{2+} did not vary in parallel to the increasing F^- contents ($R^2 = 0.0009$, data not shown).

Results suggest the occurrence of calcite precipitation processes in the aquifer which may enhance the Ca^{2+} removal in groundwater. Calcite precipitation associated to reverse cation exchange processes can occur in the NE area of the Chittur block where the presence of F^- in groundwater is higher. If data points PGT29, F19 and PGT2, which present the highest F^- contents (1.72 mg/L, 2.30 mg/L and 6.30 mg/L, respectively), are not considered, statistical results showed that F^- concentrations are to some extent positively correlated with alkalinity ($R^2 = 0.2$, data not shown) coinciding with the results of Handa (1975). Secondly, calcite precipitation maintains F^- under subsaturated conditions which induce the appearance of increasing levels of F^- contents. Due to precipitation of Ca^{2+}, the media would become more alkaline with increasing contents of Na^+ (Raju et al. 2012).

Assuming that the distribution of F^--bearing geological formations and hydraulic properties of the aquifer media can be considered homogeneous at aquifer scale, other factors such as the physico-chemical properties of the environment and the nature and extent of water-rock interaction can affect the distribution and fate of F^- in the aquifer. In the Chittur Block, the highest values of F^- contents were found in zones of the aquifer system where the water table was lowered as a consequence of overexploitation (Fig.1C). The lack of correlation of F^- with Ca^{2+} was not as good as expected due to the heterogeneous nature of the water-rock interaction processes. . The rapid response of F^- concentrations to water level fluctuation and salinization is due to the fact that fluoride chemical equilibrium can be reached in time spans lower than the residence time of groundwater. On the contrary silicates, due to their lower reaction rates, may not reach equilibrium in the same conditions (Apello and Postma, 2005).

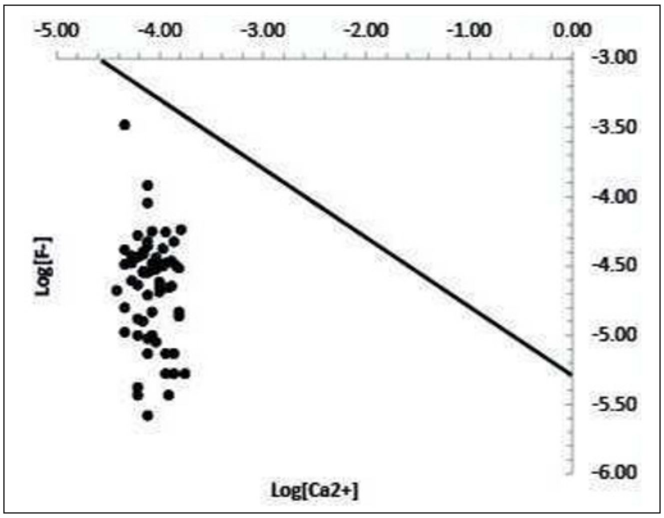

Fig.7. The stability of fluorite and the saturation of groundwater from the Chittur Block considering a LogK= -10.58, at 25º and 1 atm. of pressure.

Nitrate in groundwater

In the Chittur block, NO_3^- concentration varied from 1.4 mg/L to 141.1 mg/L (mean value of 25.3 mg/L; n = 61) which is indicative of the large differences in NO_3^- distribution in groundwater. The excess of N in the environment leads to the recharge of contaminated groundwater by NO_3^-. Nitrate recharge in the natural system is heterogeneous as suggested by the spatial distribution of this anion in groundwater (Fig.3F). The distribution and fate of NO_3^- in groundwater can be determined by several factors such as climate, the source and amount of N-species, physical properties of the hydrogeological system, relationships with other water bodies, exploitation regime, and bio-geochemical attenuation processes such as denitrification reactions. The highest concentrations were found in F44, PGT2, F18, F25, F47a, F3, PGT69, F28, and PGT48 wells (Fig.3F) and all are located very close to agricultural land, where fertilizer usage is common.

Generally, the sources of NO_3^- can be associated to agricultural, farming and urban activities. For the 2007-2008 period, about 113 km^2 (43.4% of the total surface area of the Chittur block) correspond to paddy cultivated areas. Garden land occupies about 97.4 km^2 (37.2% of the total surface area). Only 14.3 km^2 (5.5% of the total surface area) correspond to forest land. Thus, NO_3^- derived from agriculture can constitute a potential source of pollution since this land use occupies an important extension. The proximity of the water level to the surface (in some cases as low as 2 mbgs) helps contaminants reach rapidly the saturated zone of the aquifer. In this sense, it would be expected that the shallowest the sample depth the most contaminated the groundwater. However, the calculated determination coefficient ($R^2 = 0.05$) suggest the absence of correlation between NO_3^- and water level.

The resulting relationship between NO_3^- and Cl^- depends on the initial concentrations of both aqueous species in the natural system, the exploitation regime of the aquifer system and climate conditions, which control the net recharge, and the existence of natural attenuation processes of NO_3^-. If both anions can be considered as conservative species once NO_3^- reached the saturated zone, their concentrations along with the groundwater flow can result in positive NO_3^-/Cl^- correlation coefficients. In fact, the study of the relationship between NO_3^- and Cl^- contents have been proposed as a tool for elucidating sources of NO_3^- in groundwater (BGS 2003) as well as for determining if NO_3^- decline is due to dilution (mixing) or consumption processes (Mengis et al. 1999). The distribution of the samples in the scatter diagram did not show a clear trend resulting in determination coefficient ($R^2 = 0.002$; data not showed; Fig.8). The absence of relationship between NO_3^- and Cl^- concentrations can be explained by the fact that the groundwater samples were not taken along the groundwater flow line.

Mengis et al. (1999) employed the NO_3^-/Cl^-method to determine if the decreasing trends in NO_3^- concentrations is due to dilution or consumption processes. Except for three samples (F47a, F18, F3), the NO_3^-/Cl^- ratio allowed to cluster the samples into two groups. The first group (G1) of samples plotted close to the dilution line ($R^2 = 0.83$; Fig.8). Since Cl^- and groundwater level contour map are visually positively correlated it is possible to infer that the concentration of Cl^- in groundwater is enhanced by increasing withdrawal rates (Figure 1C, 3H). If the volume of groundwater abstraction is high, mixing can result in both high Cl^- and NO_3^- concentrations depending on the initial nitrate load. Therefore, the distribution of NO_3^- and Cl^- can be explained by simple dilution (mixing) or advection processes driven by mixing with irrigation return flows.

The second group (G2) are constituted by samples with relatively low NO_3^- contents (up to 22.1 mg/L in spite of the increasing Cl^- values ($R^2 = 0.05$, Fig.8). Natural attenuation of NO_3^- by biogeochemical processes can explain the NO_3^-/Cl^- trend encountered. In natural systems, heterotrophic or autotrophic denitrification reaction in anaerobic environments may decrease the presence of NO_3^- in groundwater, since microorganisms employ NO_3^- for respiration processes (see Korom,1992). Heterotrophic denitrification can be driven in the Chittur Block by the presence of labile organic matter, derived from black soil or wastewaters, for bacteria population. The pH values (6.5-8.2; average value of 7.2.) fall in the range adequate for the existence of denitrification reactions (Rivett et al. 2008) but there is no data available on the redox conditions in the system which can support the discussion. Multi-isotope studies can help understand the sources and fate of NO_3^- in the aquifer system. Additionally, if NO_3^- is employed for oxidizing organic matter, alkalinity can increase and promote calcite precipitation, which in turn favours the dissolution of fluoride-bearing minerals. During autotrophic processes denitrifying bacteria employs Fe_2S and Fe^{2+}-silicate minerals as source of energy (Korom, 1992). During NO_3^- reduction, SO_4^{2-} and Fe^{3+}would be produced. Sulphate concentration changed from 3.2 to 249.1 mg/L in the Chittur Block. Interpolated SO_4^{2-} concentrations showed a trend towards higher values in the NE area of the Chittur Block, although increasing values can be found in the southern sector of the block (Fig.3G). Visually, the isocontent maps showed a positive correlation between SO_4^{2-} and Cl^- concentrations (Fig.3G, H); in fact, SO_4/Cl gave a $R^2 = 0.5$. These results suggest that the distribution of both anions in groundwater mostly responded to the same processes. The highest values of SO_4^{2-} concentrations coincided with regions of the aquifer system where the water table was lower as a consequence of overexploitation.

Summing up, several reactive processes can explain the distribution and fate of contaminants in the aquifer coupled to decreasing potentiometric levels. The weathering of crystalline rocks by atmospheric CO_2 leads to the appearance of major ions with the predominance of Na^+ and HCO_3^-, which may be indicative of pristine groundwater. Total dissolved solids value as low as 245 mg/L can be encountered. Saline groundwater modifies the natural (and pristine) condition of the aquifer, forcing it to a new, transient, equilibrium condition. Cation exchange processes result from the system response to increasingly saline conditions and can explain the loss of Na^+ relative to Cl^-, and the progressive appearance of Ca^{2+} and Mg^{2+} in groundwater. Chloride and Mg^{2+} accumulates in groundwater and Ca^{2+} precipitates as calcite mineral. The lowering of Ca^{2+} in groundwater by calcite precipitation leads to increasing content of F^- in groundwater, as groundwater becomes unsaturated in fluorite. Dhiman and Keshari (2006) found that F^- has a negative relationship with NO_3^- and pH in Mehsana District (Gujarat, India). The arrival of F^- in the groundwater flow generated a regional F^- concentration above 6.3 mg/L (Kopanur, PGT2). Nitrate appearance in groundwater, up to 141 mg/L, is mainly related to the induced recharge driven by groundwater withdrawal, but denitrification reactions driven by organic matter degradation can play an important role in the fate of NO_3^-, attenuating concentrations in groundwater but also in the dissolution of fluorite mineral. The reactive zones are not placed in deep areas of the aquifer, since deteriorated groundwater appear at depths ranging from 1.8 mbgl to about 12 mbgl. Therefore small changes in the depth to the saturated zone of the aquifer imply progressively more deteriorated conditions which leads to higher TDS values (up to 1,963 mg/L). In addition, these processes can be enhanced during persistent drought events as the dilution effects of the natural recharge decreases in effectiveness, as noted by Singh and Mukherjee (2015).

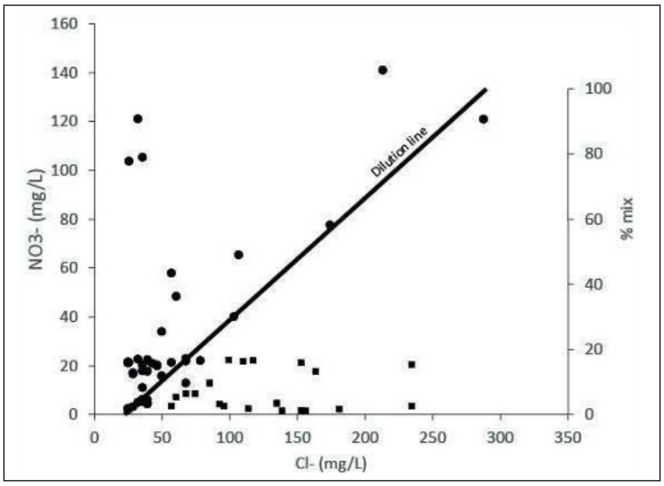

Fig.8. Chloride versus NO_3^- concentrations in groundwater samples from the Chittur Block. Group 1 of samples are represented by circles; group 2 are represented by squares.

CONCLUSIONS

The results obtained in this study show that the deterioration of water quality is closely related to the excessive use of fertilizers and the over-exploitation of groundwater resources. Hence farmers may be encouraged to switch to micro-irrigation from the current practice of flood irrigation. Adverse climatic conditions tending towards more dry conditions can lead to enhanced levels of F^-, NO_3^- and salinity in groundwater as the renewal capacity of the natural system decreases in effectiveness. This study can be a valuable guide to water managers, users and other stakeholders for the sustainable use of groundwater resources in the study area. It is recommended that groundwater abstractions should be restricted in the region.

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