Geochemical Assessment of Groundwater Around Macherla-Karempudi Area, Guntur District, Andhra Pradesh

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Abstract: Groundwater in Palnad sub-basin is alkaline in nature and Na^+ -Cl^- -HCO_3^- type around Macherla– Karempudi area in Guntur district, Andhra Pradesh. Total dissolved solids (TDS) show strong positive correlation with Cl^-, Na^+, Ca^{2+} and Mg^{2+}, and positive correlation with SO_4^{2-}, K^+ and HCO_3^-. Calcareous Narji Formation is the dominant aquifer lithology, and water-rock interaction controls the groundwater chemistry of the area. Chloro-alkaline indices (CAI) are positive at Miriyala, Adigopula, Mutukuru, Macherla and Durgi suggesting replacement of Na^+ and K^+ ions from water by Mg^{++} and Ca^{++} ions from country rock through base exchange reactions. Negative CAI values are recorded at Terala, Rayavaram and Nehrunagar, which indicate exchange of Na^+ and K^+ from the rock as cation-anion exchange reaction (chloro-alkaline disequilibrium).

TDS range from 91 to 7100 ppm (Avg. 835 ppm) and exceed the prescribed limit of drinking water around Mutukuru, Durgi, Rayavaram, Khambampadu and Ammanizamalmadaka areas. Scanty rainfall and insufficient groundwater recharge are the prime factors responsible for high salinity in the area. Fluoride content ranges from <1 to 3.8 ppm and contaminated areas were identified around Macherla (1 sq km; 3.8ppm), Mandadi (1 sq km, 2.1ppm) and Adigopula (2 sq km, <1 to 3.7 ppm). The % Na^+ content varies from 17 to 85 with the mean value of 57, and eighty (80) samples showed higher %Na^+ in comparison to the prescribed limit of 60 for irrigation water. Sodium Adsorption Ratio (SAR) and % Na^+ in relation to total salt concentration indicate that groundwater (51%) mostly falls under doubtful to poor quality for irrigation purpose. Groundwater of Adigopula village is fluoride contaminated and remedial measures are suggested to improve the water quality.

Keywords: Chloroalkaline indices (CAI), Potability, Total dissolved solids (TDS), Fluoride, Sodium absorption ratio (SAR), Macherla-Karempudi, Andhra Pradesh.

INTRODUCTION

Atomic Minerals Directorate is actively involved in the Palnad sub-basin for exploration of unconformity type uranium mineralisation. As an additional tool for subsurface exploration, hydrogeochemical sampling was carried out and water samples were analysed regularly for concentrations of various cation, anion, TDS etc (Sinha, 2004). In the present paper, with the available analytical results of samples from Macherla-Karempudi area, attempt has been made to characterize the geochemistry of groundwater and to understand the influence of aquifer lithology on the ground-water chemistry. Water quality assessment in terms of potability and irrigational use is also presented. The study area around Macherla-Karempudi sector, lying in the northeastern part of the Cuddapah Basin, is underlain by rocks of Kurnool Group. Falling between latitudes 16°20' and 16°30'N; and longitudes 79°25'and 79° 45'E, it covers an area of 400 sq km in Guntur district. Water samples were collected from the private tube wells having fairly good density, and each sample represents an area of 2 km x 2 km. Groundwater in the area is utilized for both agricultural and drinking purposes. Average depth of water table is 70 to 80 m below ground level and the aquifer lithology is carbonate rock of Kurnool Group (Nagaraja Rao et al. 1987). Hydrochemistry is discussed in order to understand water–rock interaction processes and to quantify the concentration of the inorganic constituents present in groundwater with respect to the standards of safe potable and irrigation water quality.

GEOLOGY OF THE AREA

The area exposes Dharwarian chlorite-sericite/amphibole schists, Banded Iron Formation (part of the Peddavura schist belt) and Lower Proterozoic epidotised biotite granites grouped as basement rocks, unconformably

overlain by the sub horizontal Palnad sediments, which are equivalents of Kurnool Group in the northeastern part of Cuddapah Basin (Nagaraja Rao et al. 1987, Fig.1). Basement rocks are exposed in the northwestern part of the study area with a thin cover belonging to the Kurnool Group of rocks. The Palnad sediments comprise Banganapalle quartzite/ shale, Narji limestone/calc shale, Owk shale, Paniam quartzite and Nandyal shale. The major part of the area is underlain by Narji Formation which is the dominant aquifer lithology and controls the groundwater chemistry. Calcareous Narji Formation is playing a major role in ion and base exchange reactions. South of the study area, the Cumbum Formation (ferruginous and tectonised quartz - arenite with fused grain boundaries, and calcareous, carbonaceous/graphitic phyllite) is thrusted against the Palnad sediments.

METHODOLOGY

A total of 187 water samples were collected in duplicate over 400 sq km area in a grid pattern of 2 km x 2 km in high quality polythene bottles of one litre capacity from borewells and hand pumps that were extensively used for both domestic and irrigation purpose. Sample bottles were thoroughly rinsed with the water to be sampled and then packed under airtight condition to discard the chances of entrapment of any air bubble. Watman paper was used to filter the turbid water sample to remove suspended particles, and samples were analysed in the Chemical Laboratory, Hyderabad. Volumetric method was used to analyse Ca^{2+}, Mg^{2+}, HCO_3^- and CO_3^{2-}. Cl^- and F^- were analyzed by ion-selective/volumetric method using ORION ion selective electrodes of chloride (model S4-17B) and fluoride (model 94-09) respectively. Na and K were analysed by flame photometers, total dissolved salt by gravimetric method, Si by spectrometry, SO_4^{2-} by turbidity; pH by a pH meter and conductivity by conductivity meter. Total Fe, Cu, Pb, Zn, and Mn were determined by flame atomic absorption/ emission spectrometer (AAS/AES) using Varian spectrophotometer AA-20B.

Table 1. Statistical details of chemical parameters for the analysed samples (n= 187)

| S.No	Chemical Parameters	Range	Average	Remarks
1	pH	7 – 8.5	7.8	n =187
2	Eh (mv)	83 – 310	149	n =187
3	Conductivity	120 - 9500	1371	n =187
4	Total dissolved solids (ppm)	91 - 7100	835	n =187
5	Sodium (ppm)	5 – 918	151	n =187
6	Potassium (ppm)	<1 – 947	28	n =175; (12 samples below detectable limit)
7	Calcium (ppm)	10 – 500	83	n = 187
8	Magnesium (ppm)	<5 – 222	31	n =185; (2 samples) below detectable limit
9	Bi carbonates (ppm)	40 – 830	297	n = 187
10	Carbonates (ppm)	<5 – 44	15	n =9; (178 samples below detectable limit)
11	Sulphates (ppm)	<10 - 750	120	n =182; (5 samples below detectable limit)
12	Chlorides (ppm)	<10 - 2130	193	n =185; (2 samples below detectable limit)
13	Fluoride (ppm)	<1 – 3.8	1.13	n =52; (135 samples below detectable limit)
14	Silica (ppm)	6 – 120	21	n = 187
15	Iron (ppm)	<0.005 – 8.5	0.70	n =171; (16 samples below detectable limit)
16	Manganese (ppm)	<0.010 – 1.08	0.092	n =73; (114 samples below detectable limit)
17	Copper (ppm)	<0.005 – 0.072	0.016	n =69; (118 samples below detectable limit)
18	Lead (ppm)	<0.010 – 0.060	0.033	n =7; (180 samples below detectable limit)
19	Zinc (ppm)	<0.005 – 3.90	0.227	n =157; (30 samples below detectable limit)
20	Sodium Adsorption Ratio (SAR)	1.38 – 53.90	20.56	n= 187
21	Percentage sodium (% Na $^+$)	17.39 – 85.18	57.65	n= 187
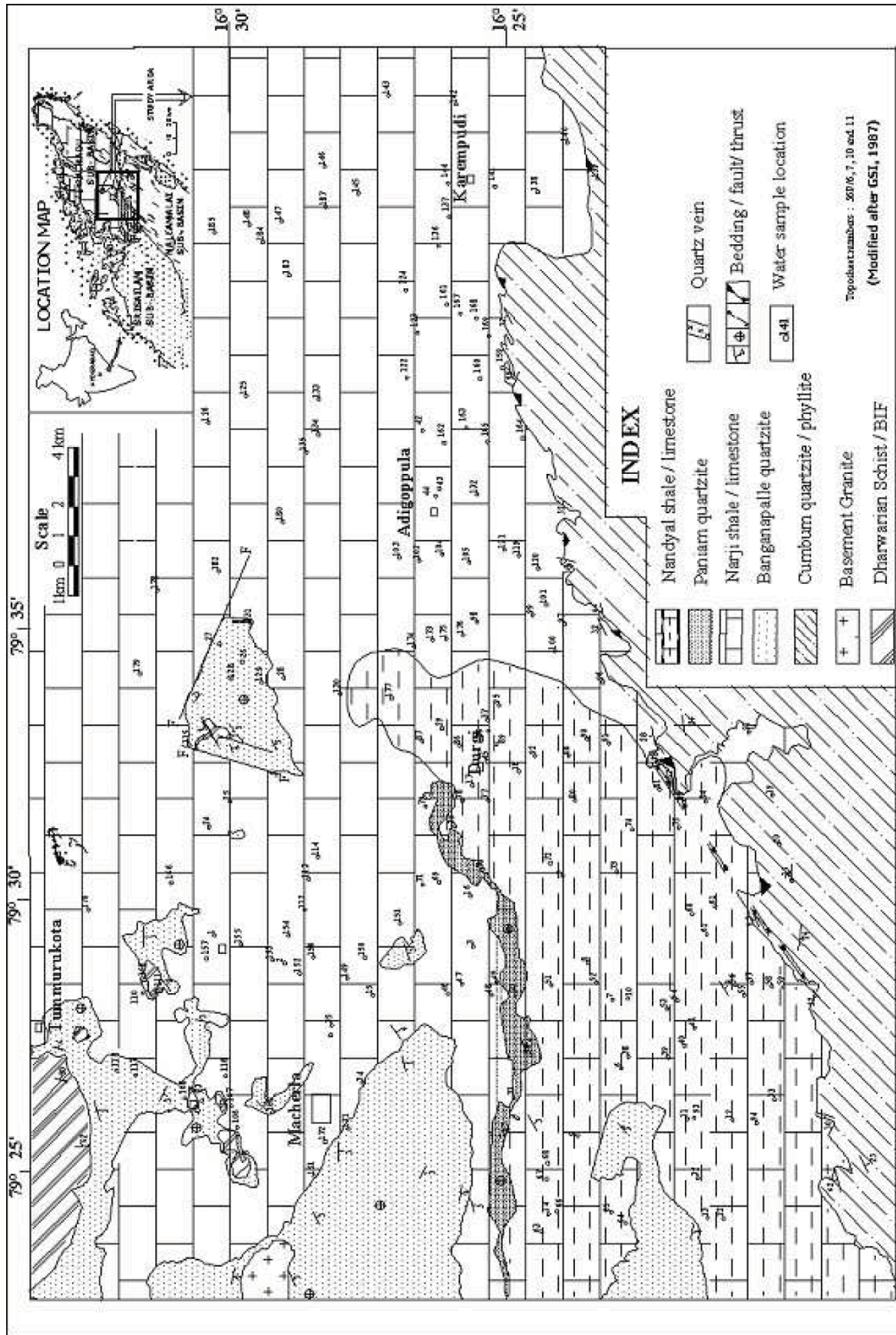
Fig.1. Geological map of Macherla-Karempudi area, Guntur district, Andhra Pradesh.

Results of Chemical Analysis

Based on the analytical results (n=187), standard chemical parameters i.e. pH, Eh, TDS, hardness, conductivity, bicarbonate, carbonate etc were calculated and presented in Table 1. pH value of the water ranges from 7.8 to 8.5 and Eh ranges from 83 to 310 milli volts indicating its alkaline nature. Conductivity ranges from 120 to 9500 m mhos and TDS varies from 91 to 7100 ppm indicating moderate to high salinity water. The saline groundwater condition is possibly attributed to low seasonal rainfall and insignificant groundwater recharge. Correlation matrix for the various parameters (Table 2) was calculated with respect to pH and TDS contents to understand the salinity and hardness of groundwater. Total dissolved solids (TDS) show strong positive correlation (r= 0.86 to 0.95) with Cl^-, Na^+, Ca^{2+} and Mg^{2+} and moderate positive correlation (r= 0.47 to 0.74) with SO_4^{2-}, K^+ and HCO_3^-.

Concentrations of Na, K, Ca and Mg vary from 5 to 918 ppm (avg. 151 ppm), <1 to 947 ppm (avg. 28 ppm), 10 to 500 ppm (avg. 83 ppm) and <5 to 222 ppm (avg. 31 ppm) respectively indicating Na^+ and K^+ as the dominant cations in the water samples. The contents of HCO_3^-, Cl^- and SO_4^{2-} were 40 to 830 ppm (avg. 297 ppm), <10 to 2130 ppm (avg. 193 ppm) and <10 to 750 ppm (avg. 120 ppm) respectively. HCO_3^- and Cl^- are the dominant anions present in the water samples. Fe, Mn, Cu and Zn are the major metallic ions present in the water samples and their contents are in the ranges of <0.005 -8.5 ppm (avg. 0.70 ppm), <0.010 - 1.08 ppm (avg. 0.092 ppm), <0.005 - 0.072 ppm (avg. 0.016 ppm) and <0.005 - 3.90 ppm (avg. 0.227 ppm) respectively. CO_3^- and Pb values are below detectable limits for most of the samples. Inter-relation between the major ion chemistry for the set of analysed samples (n=187) is given in Table 2. Ternary plots (Piper, 1944) for major cations (Mg^{2+}, Ca^{2+}, Na^+, K^+) and anions (SO_4^{2-}, HCO_3^-, Cl^-) in water samples reveal that the samples are Na^+ - $Cl^-HCO_3^-$ dominant (Fig.2).

Bicarbonate dominance may be related to dissolution and leaching process of calcareous aquifer rocks belonging to Narji Formation (Lloyd and Heathcote, 1985) as indicated by the sulphate – chloride relationship plot (Fig.3). Na^+ ions have been introduced into the system by ion exchange reaction between the calcium ions present in water, as sodium ion adsorbed by the argillaceous component of the aquifer rocks.

Gibbs' ratio (Gibbs, 1970) for major cations (Na+K/ Na+K+Ca) and major anions (Cl / Cl+HCO$_3$) of the water samples were plotted separately against respective values of total dissolved solids (Fig.4). The major ion chemistry together with Gibbs ratio plot indicates that the chemistry of groundwater in the area is controlled mainly by the chemical interaction between aquifer rocks and groundwater, and to some extent by processes like evapo-transpiration etc. The extent of interaction, however, depends upon factors like residence time of water within the aquifer, topographic condition, continuous irrigation practices and anthropogenic (fertilizers and sewage wastes) activities. The annual rainfall and groundwater recharge of the area are insignificant; the process of evaporation might have incorporated some components of sodium and chlorine ions.

Chloro-alkaline indices, CAI 1 = Cl- (Na+K) / Cl and CAI 2 = Cl – (Na+K) / SO_4+HCO$_3$ + CO$_3$ + NO$_3$ (Schoeller, 1977) were calculated to study the process of ion exchange between the groundwater and its host environment during rock-water interaction. Positive CAI values noted in Mutukuru, Macherla and Durgi areas suggest that sodium and potassium from water are exchanged with magnesium and calcium in rock following base exchange reactions (chloro-alkaline equilibrium), whereas negative CAI values noted at Oppicherla, Adigopula suggest that magnesium and calcium from water are exchanged with sodium and potassium in rock favouring cation-anion exchange reactions (chloro-alkaline disequilibrium). Overlapping CAI positive and negative values were also seen especially in the areas

Table 2. Correlation coefficient matrix of chemical data of groundwater (n=187)

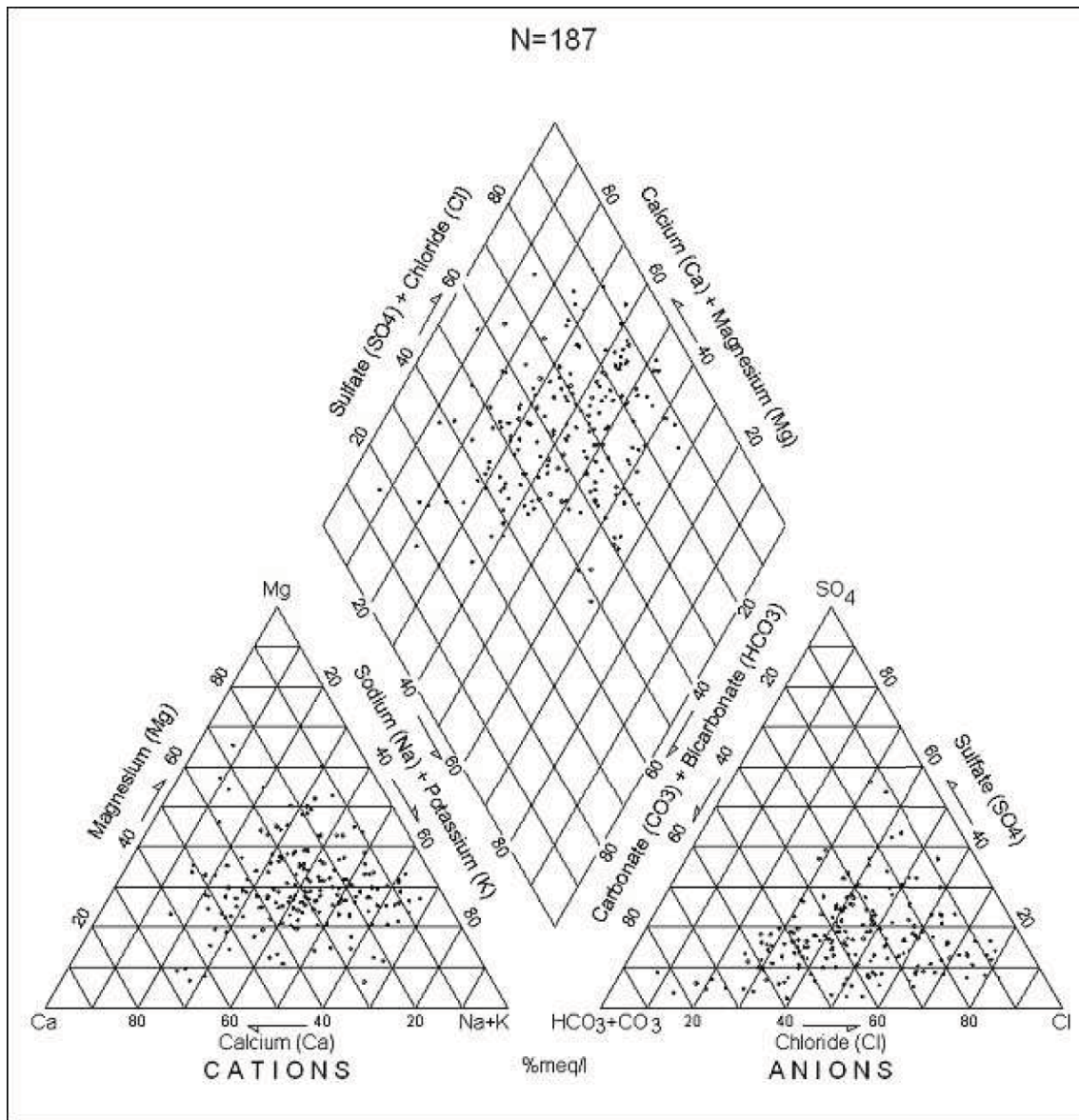|	pH	TDS	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	Cl^-	SO_4^{2-}	F^-
pH	1.00									
TDS	-0.33	1.00								
Ca^{2+}	-0.48	0.87	1.00							
Mg^{2+}	-0.25	0.86	0.75	1.00						
Na^+	-0.17	0.90	0.67	0.74	1.00					
K^+	-0.08	0.71	0.46	0.53	0.59	1.00				
HCO_3^-	-0.29	0.47	0.46	0.43	0.47	0.39	1.00			
Cl^-	-0.25	0.95	0.79	0.88	0.87	0.70	0.38	1.00		
SO_4^{2-}	-0.16	0.74	0.63	0.53	0.79	0.52	0.25	0.67	1.00	
F^-	0.11	-0.0001	-0.01	0.05	0.05	-0.03	0.08	0.01	0.03	1.00

Fig.2. Piper diagram for ionic composition of water samples (*after* Piper, 1944).

around Ammanizamalmadaka, Khambampadu and Cheragudipadu, which indicate both base exchange and cation-anion exchange reactions. Location map of samples with CAI values are shown in Fig.5.

Potability of Groundwater

Parameters to assess groundwater potability were compared with specifications of World Health Organisation (WHO, 1984) and Bureau of Indian Standards (BIS, 1991) in Table 3 and are discussed as follows.

pH

Groundwater is slightly alkaline with average pH of 7.8

(n=187), which shows moderate negative correlation coefficient with major cations Ca^{++}, Mg^{++}, Na^+, K^+ and anions Cl^-, SO_4^-. pH of groundwater of the area has no adverse effect on human health.

Total Dissolved Solids (TDS)

TDS in groundwater varies from 91 to 7100 ppm (avg. 835 ppm). On comparison with the drinking water standards, it was observed that 19% samples analysed have TDS concentrations greater than the prescribed limits in and around Mutukuru (29 sq km area), Durgi (4.32 sq km area), Rayavaram (5.12 sq km area), Khambampadu (4.60 sq km area) and Ammanizamalmadaka (10.24 sq km area) villages.
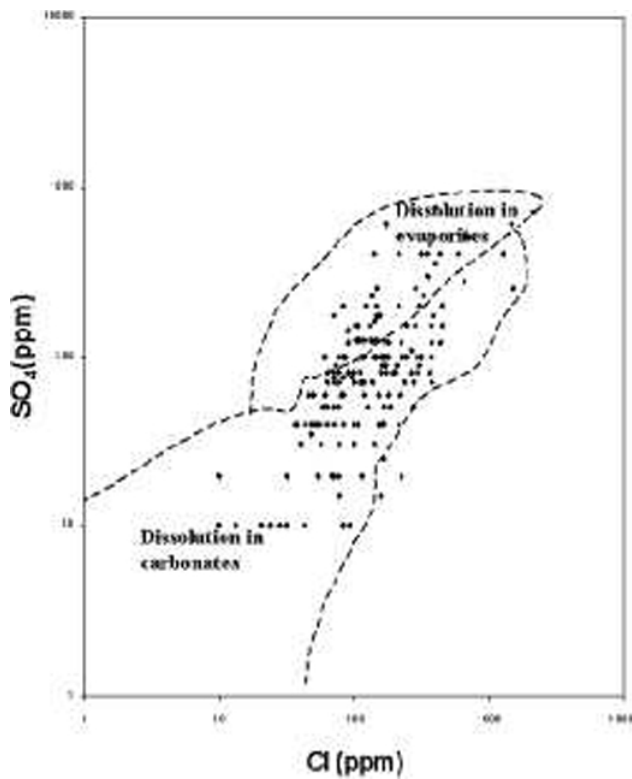
Fig.3. Sulphate-Chloride relationship plot for water samples from the study area (*after* Lloyd and Heathcote, 1985).

Table 3. Drinking water quality standards

Parameters	BIS (1991)	WHO (1984)	Analysed samples from Macherla- Karempudi area (n=187)	
			Range	Percentage of samples beyond desired limits
pH	7.0 - 8.5	6.5 - 8.5	7.0 – 8.5	-
Total dissolved solids (ppm)	500	1000	91 - 7100	19
Hardness (ppm)	300	-	83 - 2256	35
Calcium (ppm)	75	500	<10 - 500	43
Magnesium (ppm)	30	-	<5 - 222	28
Sodium (ppm)	-	200	<5 - 918	21
Bicarbonates (ppm)	300	-	40 - 830	43
Chlorides (ppm)	250	250	<10 - 2130	19
Sulphates (ppm)	150	400	<10 - 750	9
Fluorides (ppm)	0.6-1.2	1.5	<1 – 3.8	9
Copper (ppm)	2.0	2.0	<0.005 – 0.072	nil
Zinc (ppm)	3.0	3.0	<0.005 - 3.90	1
Lead (ppm)	0.01	0.01	<0.010 – 0.060	4
Iron (ppm)	1.0	2.0	<0.005 - 8.5	55
Manganese (ppm)	0.4	0.5	<0.010 – 1.08	1

Scanty rainfall, evaporation and insufficient groundwater recharge are the prime causes of salinity. Hardness of water is due to calcium, magnesium and bicarbonate contents. High TDS (>1000ppm) exceeding the limit of potable water standard causes gastro-intestinal irritation.

Iron

Iron in groundwater ranges from <0.005 to 8.5 ppm with an average of 0.70 ppm. The prescribed limit of iron content in potable water is up to 2 ppm. In the present study, 55% of the total samples analysed have iron contents higher than
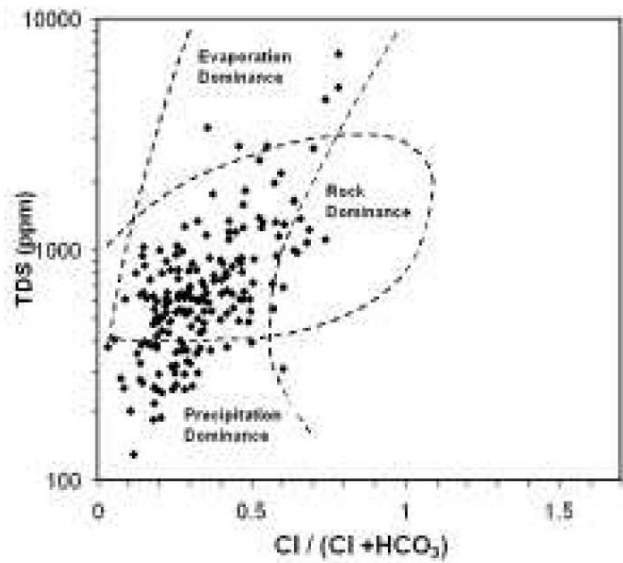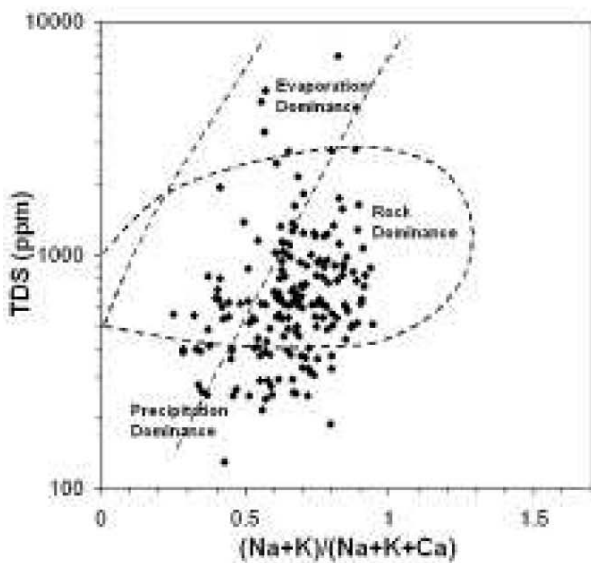

Fig.4. Mechanism controlling chemistry of groundwater (*after* Gibbs, 1970).
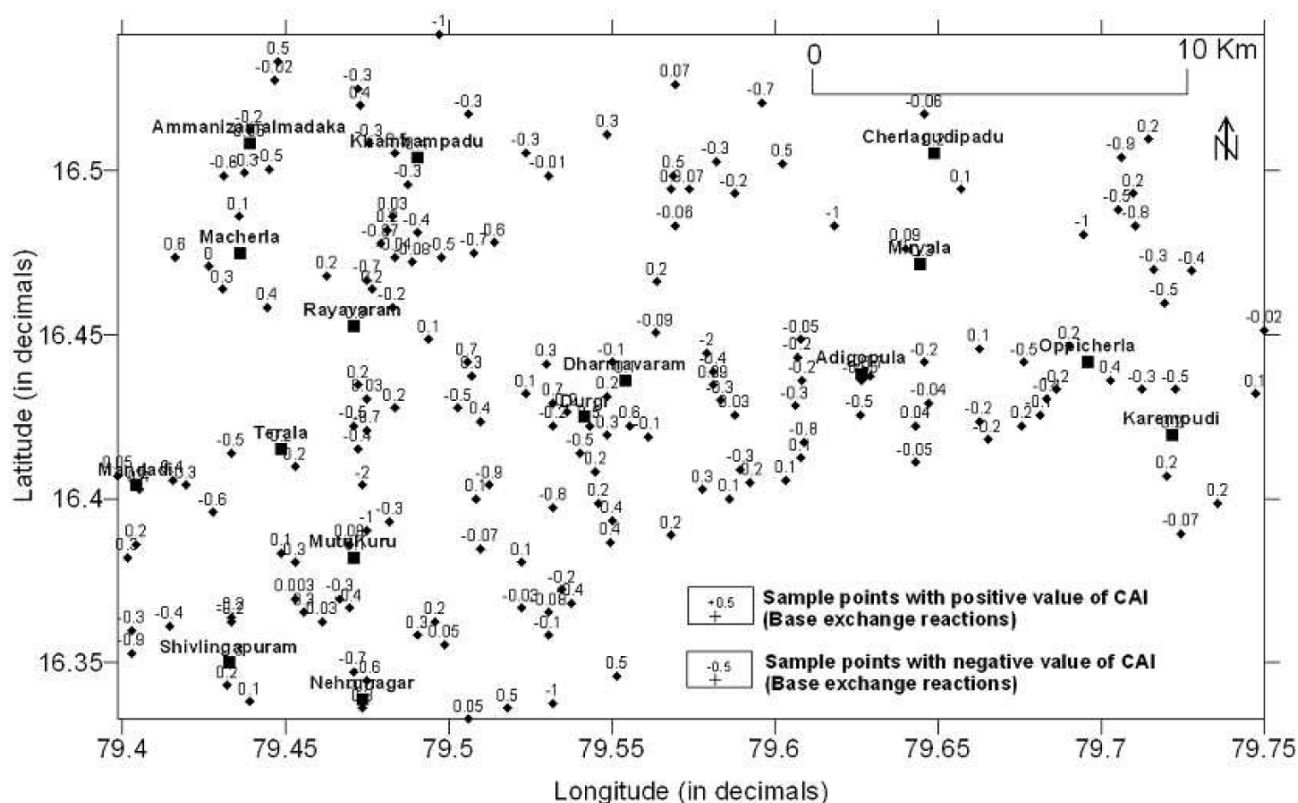
Fig.5. Sample location map showing values of chloroalkaline index (CAI-1) in Macherla-Karempudi area.

the desired limit, particularly around Macherla, Durgi and Mutukuru.

Fluoride

The fluoride content of groundwater is in the range of <1 to 3.8 ppm with an average of 1.4 ppm. Excess of fluoride causes 'mottled enamel' in teeth, disfiguration of teeth and crippling of bones. However, concentration below or up to 1.25 ppm in water is beneficial for teeth. Areas with semi-arid climate, crystalline rocks and alkaline soils are mainly affected by fluoride contamination (Handa, 1975). The area is overall free from fluoride contamination, except around Macherla (1 sq km, 3.8 ppm, n =1), Mandadi (1 sq km, 2.1 ppm) and Adigopula (2 sq km, <1- 3.7 ppm, n=7) villages (Fig.6).

Copper, manganese and zinc contents in the ground-water are within the prescribed limits of potable drinking water.

Water Quality for Irrigation

The suitability of water for irrigation purpose depends on the sodium ion and total salt content of the water. Plants intake water from soil by osmosis and osmotic pressure is proportional to the salt content, which affects the growth of plants, soil structure and permeability. Concentrations of soluble salts in irrigation water can be expressed as low (EC<250 μS/cm), medium (250 to 750 μS/cm) and very high (EC>2250 μS/cm) salinity zones (Richards, 1954). Higher EC in water generates saline soil and higher Na^+ develops alkaline soil. The sodium or alkali hazard is expressed in terms of sodium adsorption ratio (SAR) as below;

$$SAR = (Na^+/ \{[Ca^{2+} + Mg^{2+}] /2\}^{0.5})$$

If the water used for irrigation is high in Na^+ content and low in Ca^{2+}, ion exchange of Na^+ with Ca^{2+} and Mg^{2+} in soil destroys the soil structure due to the dispersion of clay particles (Table 4). Data plot (Fig.7) on the US salinity diagram (Richards, 1954) shows that 51% of the groundwater samples under study falls in high to very high SAR domain and hence is of poor quality for irrigation purpose (Table 4). Percentage Na^+ is another important parameter (Wilcox, 1955) for assessment of suitability of water quality for irrigation, which is expressed as;

$$\% Na^+ = (Na^+ + K^+) \times 100/ (Ca^{2+} + Mg^{2+} + Na^+ + K^+)$$

The values of %Na^+ in the analyzed samples vary from 17 to 85 with a mean value of 57. Prescribed limit for %Na^+ in irrigation water is 60 (Subba Rao and John Devadas,
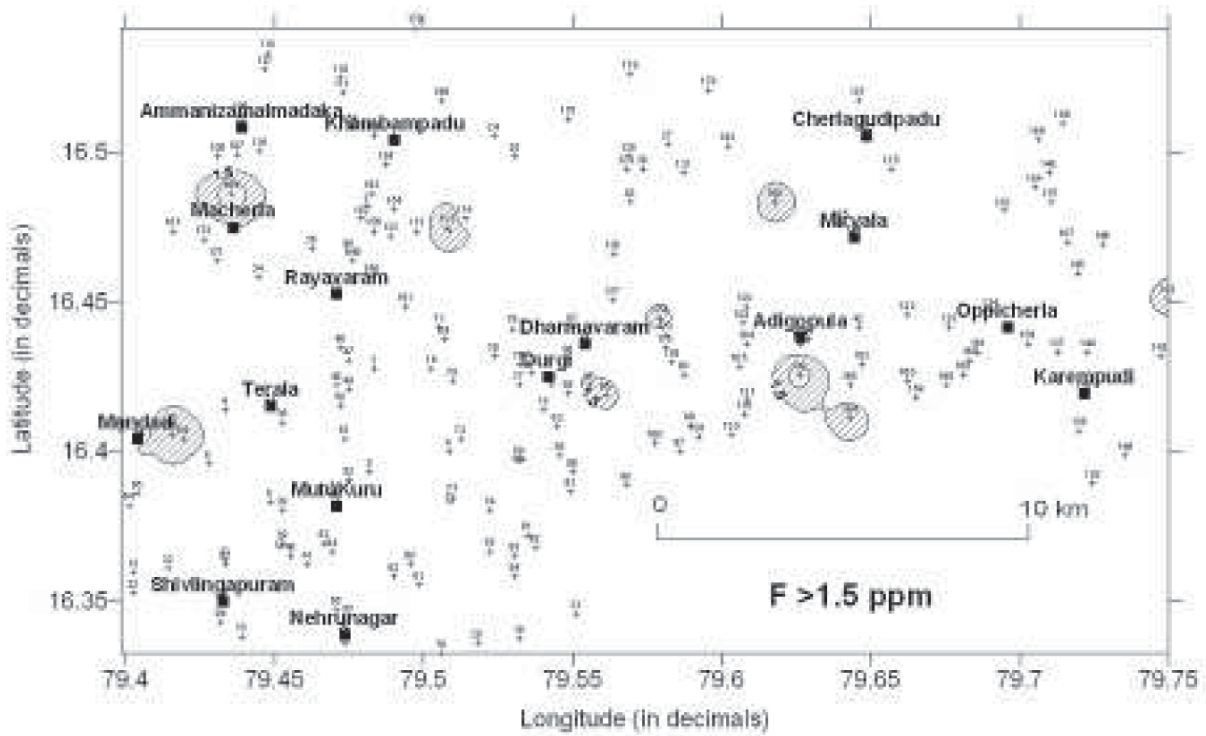
Fig.6. Contour map showing areas with fluoride hazard in Macherla-Karempudi area.
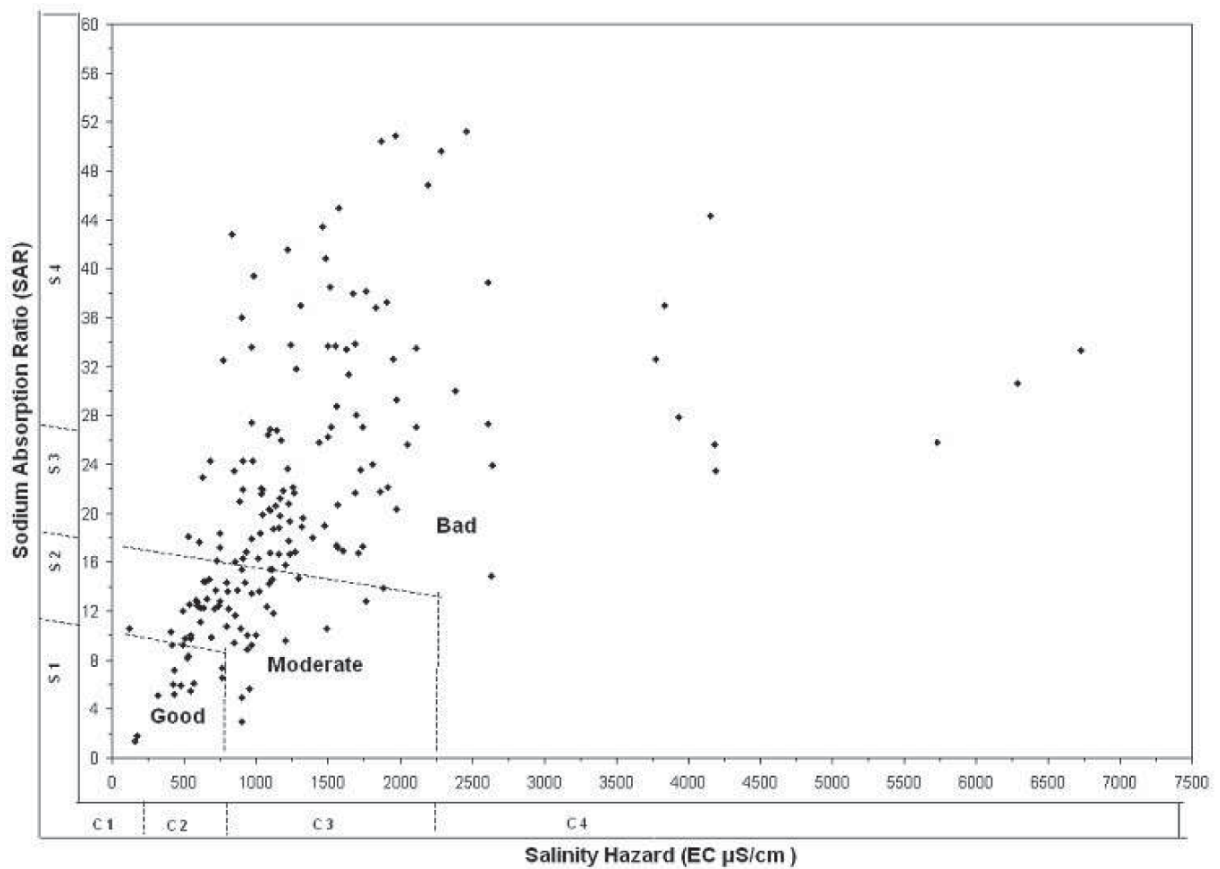

Fig.7. Classification of groundwater for irrigation - USSL diagram (*after* Richards, 1954), Macherla-Karempudi area.

**Table 4.** Classification of degree of risk of using groundwater for irrigation (Richards, (1954)

Class	Description	Class	Description
C 1	Low salinity water (EC< 250 μS/cm) can be used for most crops on most soils with little likelihood of soil salinity development. Some leaching is required, but this occurs under normal irrigation practices except in soils of extremely low permeability.	S 1	Low sodium water (SAR< 6) can be used for irrigation on most soils with little danger of developing harmful levels of exchangeable sodium.
C 2	Medium salinity water (EC: 250- 750 μS/cm) can be used if a moderate amount of leaching occurs. Crops of moderate salt tolerance can be irrigated with this water without special practice.	S 2	Medium sodium water (SAR: 6 - 12) will present an appreciable sodium hazard in fine textured soil, especially poorly leached soils. Such water may be safely used on coarse textured or organic soils with good permeability.
C 3	High salinity water (EC: 750 - 2250 μS/cm) cannot be used on soils of restricted drainage. Even with adequate drainage, special management for salinity control may be required and crops of good salt tolerance can be selected.	S 3	High sodium water (SAR: 12 - 18) may produce harmful levels of exchangeable sodium in most soils and will require special soil management such as good drainage, leaching and addition of organic matter.
C 4	Very high salinity water (EC > 2250 μS/cm) is not suitab suitable as irrigation water under ordinary circumstances. It can be used only on crops that are very salt tolerant and only if special practices are followed, including provision for high degree of adverse effects.	S 4	Very high-sodium water (SAR >18) is generally unsatisfactory for irrigation unless special action is taken, such as addition of gypsum to soils.

2005), and eighty samples (42.8%) show higher %Na⁺ (>60). Based on the permissible limits of SAR and % Na⁺ values, areas with groundwater quality suitable for irrigation are demarcated (Fig. 8; SAR <18 and %Na⁺ <60).
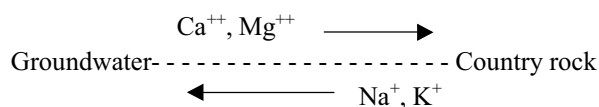
CONCLUSIONS

Groundwater of Macherla-Karempudi sector is alkaline in nature and of Na^+- $Cl^-HCO_3^-$ type. Narji Formation is the dominant aquifer lithology. Interaction between the calcareous aquifer rocks and the groundwater, controls the groundwater chemistry of the area, which is mainly attributed to:

a) Exchange of sodium and potassium in water with magnesium and calcium in rocks (base exchange reaction).

$$\text{Groundwater} \underset{\longleftarrow Ca^{++}, Mg^{++}}{\overset{Na^+, K^+ \longrightarrow}{\text{- - - - - - - - - - - - - - - -}}} \text{Country rock}$$
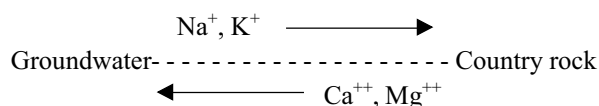
b) Exchange of magnesium and calcium in water with sodium and potassium in rock (cation- anion exchange reaction).

$$\text{Groundwater} \underset{\longleftarrow Na^+, K^+}{\overset{Ca^{++}, Mg^{++} \longrightarrow}{\text{- - - - - - - - - - - - - - - -}}} \text{Country rock}$$

Bicarbonate dominance may be related to dissolution and leaching of the calcareous aquifer rocks (Narji

limestone/ shale). Dominance of Na⁺ ion may be due to ion exchange reaction between the calcium ions present in water or the sodium ion adsorbed by the silt/ clay layers in Narji Formation.

In terms of potability, although concentrations of many parameters are within the desired limits of drinking water quality (WHO, 1984; BIS, 1991), the groundwater of the area is affected by excess salinity and iron content. This can cause gastrointestinal problems to the local population. Excess salinity affects the potability of groundwater. In areas where fluoride content is high as around Macherla (3.8 ppm), Mandadi (<1-2.1ppm) and Adigopula (<1 – 3.7 ppm) villages, remedial measures are needed.

Based on the values of SAR and % Na⁺ in relation to total salt concentration, groundwater is categorized as of doubtful to poor quality for irrigation purpose. Around 51% of the samples belong to high saline water class and has high SAR making them unfit for irrigation. The following remedial measures (Subba Rao and John Devadas, 2005) can be effective in the study area.

   i) Drip irrigation practices to prevent leaching and weathering of aquifer rocks.
  ii) Application of calcium chlorite, gypsum and organic manures to cause de-alkalisation and deflocculation, and generate more permeable soil to support plant growth.
 iii) Use of Rainwater harvesting techniques to reduce the fluoride content.
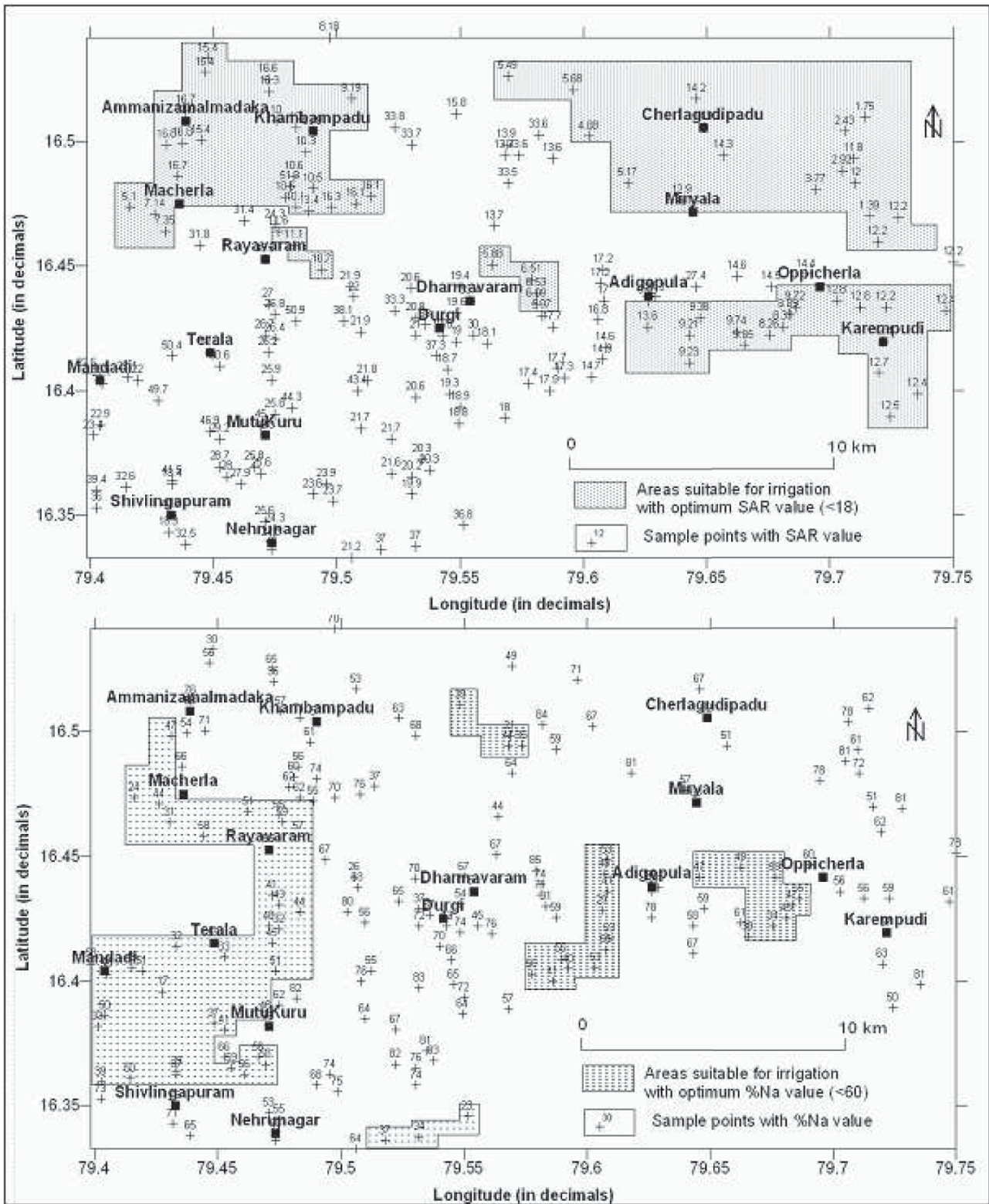 iv) Cultivation of sodium salt tolerant crops.

Fig.8. Areas suitable for irrigation based on sodium adsorption ratio and percentage of sodium values.

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