

Hydrogeochemical Characterisation of Groundwater in Salem District of Tamilnadu, India

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Abstract: The Salem district, located in semi arid southeast India, is an important industrial and agricultural center. In recent years rapid development has created an increase in demand for groundwater. Detailed knowledge of water quality gives a brief insight on the hydrochemical system, promoting sustainable development and effective management of groundwater resources. A hydrogeochemical investigation was conducted in the Salem district by collecting a total of 108 groundwater samples for Pre and Post monsoon seasons. The study reveal that pH in the area is neutral to alkaline ranging from 6.6 to 8.6 with an average of 8.0. The electrical conductivity and total dissolved solids (TDS) values was noted higher during both the seasons. The abundance of major ions in the groundwater is in the order of Na > Ca > Mg > K=Cl>HCO₃>SO₄>NO₃. Hydrochemical facies demarcated was Ca-Mg-Cl, Na-Cl, Ca-HCO₃, Ca-Na-HCO₃ and Ca-Cl type. NO₃, Cl, SO₄ and F exceed the permissible limit during both the seasons. The quality of groundwater has been assessed by using SAR, Permeability Index and RSC values along with Wilcox and USSL diagrams. As per the classification of water for domestic and irrigation purposes, the influence of anthropogenic activities such as intense agricultural practices like application of fertilizers, irrigation practice, urban and industrial waste discharge influence the quality of groundwater in the study area.

Key words: Salem, hydrogeochemical facies, sodium adsorption ratio, residual sodium carbonate and spatial distribution

INTRODUCTION

The monitoring of water quality is one of the important tools for sustainable development and provides important information for water management. Groundwater quality is based upon the physical and chemical soluble parameters due to weathering from source rocks and anthropogenic activities. In general, the quality of groundwater depends on the composition of recharge water, the interaction between the water and the soil, the soil-gas, the rock with which it comes into contact in the unsaturated zone, and the residence time and reactions that take place within the aquifer (Freeze and Cherry, 1979; Hem, 1989; Fetter, 1990; Appelo and Postma, 2005). Thus, the principal processes that influence the quality of water in an aquifer are physical, geochemical and biochemical. Changes in the concentrations of certain constituents due to natural or anthropogenic causes may alter the suitability of groundwater. Assessing groundwater quality and developing strategies to protect aquifers from contamination are necessary aspects for proper planning and designing water resources. The importance of water

quality in human health has recently attracted a great deal of interest. In developing countries like India around 80% of all diseases are directly related to poor drinking water quality and unhygienic conditions (Olajire and Imeokparia, 2001; Prasad, 1984). Anthropogenic activities like explosion of population, industrial growth, inputs of fertilizer, pesticides, and irrigation has been a crucial factor for determining the quality of groundwater. Numerous publications have reported that urban development and agricultural activities directly or indirectly affect the groundwater quality (Jalali, 2005a; Rivers *et al.*, 1996, Kim *et al.*, 2004, Srinivasamoorthy *et al.*, 2009, Goulding, 2000; Pacheco and Cabrera, 1997).

The usage of groundwater has increased substantially in Salem district of Tamilnadu, India. Hence, it is necessary to undergo for quality analysis of groundwater in order to assess its suitability for consumption, irrigation and industrial activities. An appropriate assessment of the suitability of groundwater for domestic water supplies requires the concentrations of some important parameters like pH, electrical conductivity (EC), total dissolved solids (TDS), Ca, Mg, K, Na, Cl, HCO₃, SO₄, F, NO₃, and PO₄, and comparing with the guideline values set for

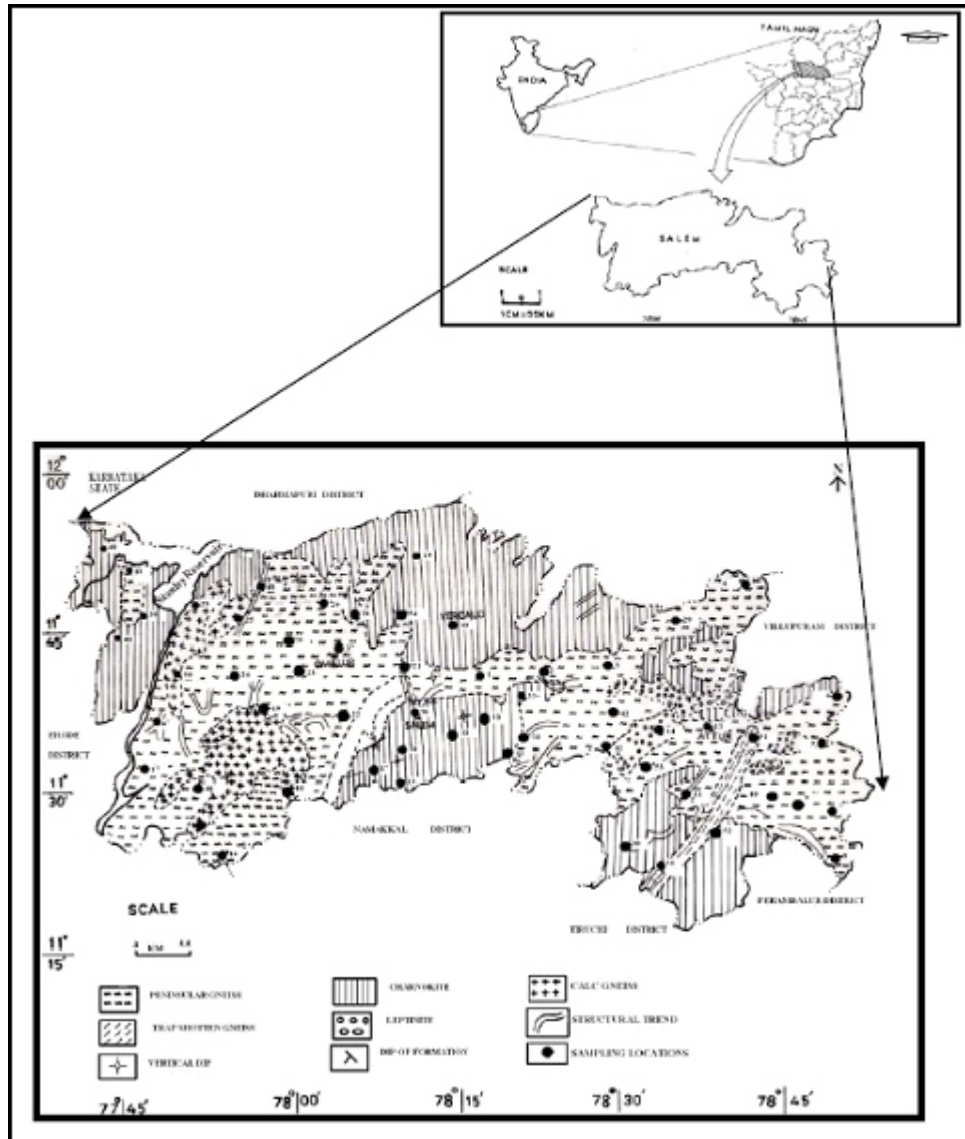


Fig. 1: Location, geology and groundwater sampling points of the study area

potable water (WHO, 1996; ISI, 1995). Irrigation water quality refers to the kinds and amounts of salts present in the water and their effects on crop growth and development. High salt concentrations influence osmotic pressure of the soil solution and affect the ability of plants to absorb water through their roots (Glover, 1996). However, an appropriate evaluation of the water quality prior to its use in irrigation will help in arresting any harmful effect on plant productivity and groundwater recharge. The suitability of water for irrigation is determined in several ways including the degree of acidity or alkalinity (pH), EC, residual sodium carbonate (RSC), sodium adsorption ratio (SAR), Permeability Index (PI) and Total Hardness (TH) along with the effects of specific ions (Yidana *et al.*, 2008a). In general, the assessment of water quality criteria is based on the consideration of the

following related aspects like, the possible effects on the physico-chemical properties of the soil, and the impact on crop yield. In Salem, a detailed geochemical study was carried out for two seasons in order to identify groundwater quality and its suitability for domestic use by comparing the concentrations of selected water quality parameters. In addition SAR, PI, RSC and EC have been used to classify the groundwater samples for irrigation usage along with TDS and TH for industrial purposes.

Study area: The study area lies between latitudes 11°19' and 11°57' and longitudes 77°38' and 78°51' and is shown in Fig. 1. The area occupies about 5207 sq.km with a mean altitude of 1,300 m.a.s.l. The climate of the study area is semi arid, with annual precipitation ranging from 504.6 – 920.8 mm. The mean annual temperature varies

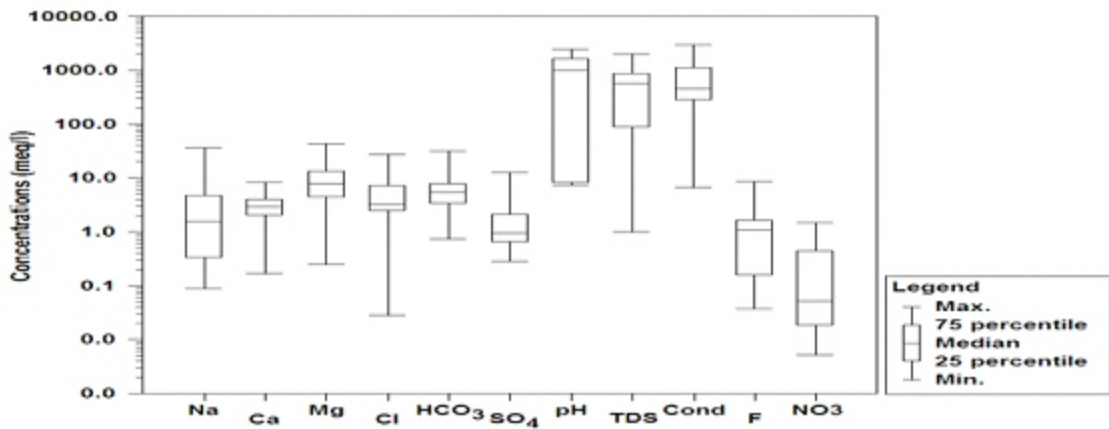


Fig. 2: Box plots for PRM and POM seasons

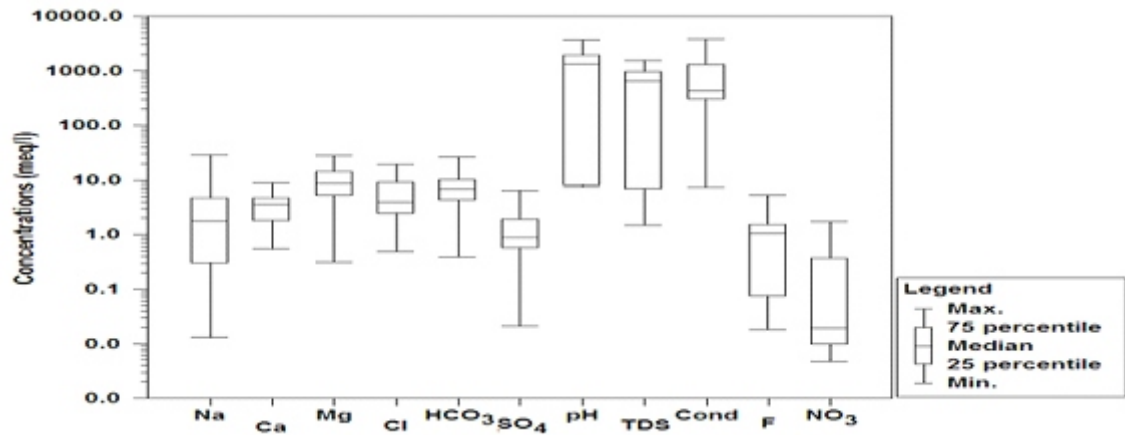


Fig. 3: Hill Piper plot for the study area

Table.1: Statistical parameters for ground water during Pre and Post monsoon seasons

Parameters	Maximum		Minimum		Average		Standard Deviation	
	PRM	POM	PRM	POM	PRM	POM	PRM	POM
pH	9	8	7	7	8	8	7.89	7.12
EC	2965	3800	222	453	1566	1790	536	733
HCO ₃	976	979	5	226	406	415	180	125
CL	975	929	31	65	286	357	201	233
SO ₄	160	184	1	18	90	93	40	43
PO ₄	5	3	0	0	1	0	1	1
NO ₃	162	83	14	1	39	31	21	17
F	7	3	0	0	2	1	2	1
H ₄ SiO ₄	52	36	3	4	26	24	11	7
Ca	130	205	3	24	60	94	28	47
Mg	484	158	21	21	75	67	68	31
Na	834	656	33	47	213	175	184	104
K	384	81	1	0	32	13	68	17
TDS	1980	1704	179	262	820	856	370	376
%Na	79	87	10	16	49	42	1	24
RSC	11	12	36	15	6	3	3	3
SAR	5	19	0	1	2	4	0	4
CR	0	0	0	0	0	0	0	0
TH	890	1130	129	188	437.2	509	189.7	204
PI	85	99	12	33	58	58	1	12

PRM –Pre Monsoon , POM-Post Monsoon, All values in mg/l except EC and pH in µs/cm, SAR- Sodium Adsorption ratio, RSC – Residual sodium Carbonate, CR – Corrosivity ratio, TH – Temporary Hardness, PI – Permeability Index

between 20 and 35° C. Shallow pediments, bajadas and denudational landforms comprise the geomorphology. The investigated area is underlain by rocks like peninsular gneiss, charnockite, ultramafic complex and potassic members confined to Archean crystalline metamorphic complexes (Fig. 1). Lineaments trending NE-SW and NW-SW with a dip angle of 45° to 75° are noted in the study area. Red insitu, red colluvial, black, alluvial, brown and mixed soils are the dominant soil types identified. The drainage is contributed by two major river systems, cauvery which flows due north south and vellar along the northwestern part. Development of groundwater is through open dug wells (shallow wells and bore wells (deep wells). Groundwater occurs in the weathered residium under unconfined conditions as well as in the fractured rocks under semi confined conditions. The depth of weathering ranges from 2.2 to 50 m, while the fractures in rocks extend to 100 m depth (Srinivasamoorthy *et.al.* 2008). Most of the dug wells are confined to the weathered zone, while the bore wells extends into the fractured zone. The water table depth reaches lowest 0.2m during monsoon (August-January) and falls below 13.5 m during summer (March-June).

MATERIALS AND METHODS

Fifty four groundwater samples were collected in one liter polyethylene bottles during Post monsoon (POM) and Pre monsoon (PRM) seasons during January and march respectively to broadly cover the seasonal variations. A total of 108 samples were collected for two seasons. Great care was taken for the spatial distribution of the samples. The selected wells are used for domestic, agricultural and industrial purposes. The samples were filtered using 0.45µ Millipore filters and analyzed for chemical constituents by using standard procedures (APHA, 1995) within 48 h of collection. The pH and electrical conductivity (EC) were measured using pH and electrical conductivity meters. Calcium (Ca) and magnesium (Mg) were determined titrimetrically using standard EDTA. Chloride was determined by standard AgNO₃ titration. Bicarbonate (HCO₃) was determined by titration with HCl. Sodium (Na) and potassium (K) were measured by flame photometry, sulfate (SO₂) by spectrophotometer turbidimetry. Phosphate was analyzed by ascorbic acid method. Nitrate and F was determined by Consort electro chemical analyzer (C960). Charge

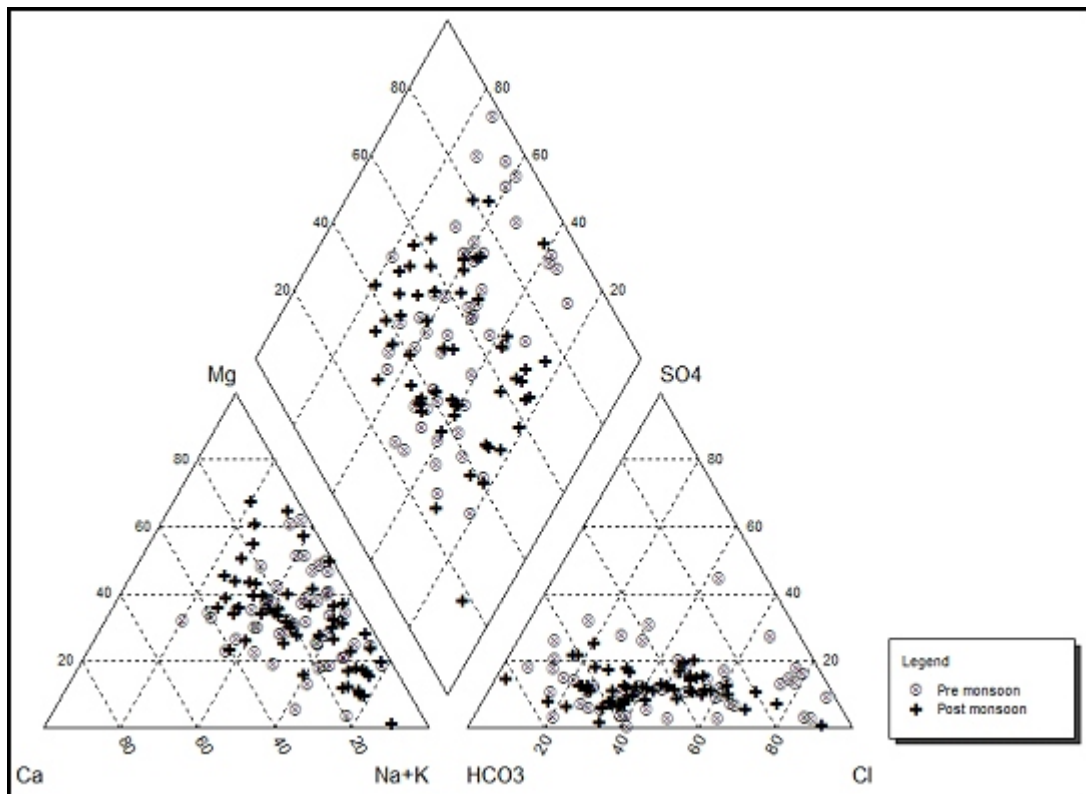


Fig. 4: Spatial distribution of TDS from the study area

Table 2: Comparison of groundwater quality with standards

Parameters	WHO (1996)	Highest desirable	Maximum Permissible		
			ISI (1995)	PRM (n=54)	POM (n=54)
pH	6.5-8.5	7.5-8.5	6.5-9.2	6.6-8.6	7.2-8.4
EC	1400.0		-	221-2965	453-3800
TDS	1000.0	500	1500.0	179-1980	261-1703
Ca	500.0	75	200.0	3-130	23-205
Mg	-	30	100.0	20-483	21-158
Na	200.0	-	-	33-834	41-655
K	-	-	-	1-384	0.30-80
HCO ₃	-	300	600.0	4-976	226-979
CL	250.0	250	1000.0	30-974	64-929
SO ₄	400.0	200	400.0	0.65-665	17-183
NO ₃	45.0	-	45.0	13-162	1.0-83
F	1.0	1.5	1.5	0.40-7.00	0.31-3.44
TH	100.0	500	150.0	129-890	187-1129

Table 3: Classification of groundwater based on drinking and agricultural utilities

TDS (mg/l)	Water classification	Seasons	
		PRM (n=54)	POM (n=54)
<1000	Fresh water	38	39
1000-10000	Brackish water 16	15	
10000-100000	Saline water	Nil	Nil
>100000	Brine water	Nil	Nil
Total Hardness as CaCO₃ (mg/l)	Water classification	PRM	POM
<75	Soft	38	39
75-150	Moderately Hard	16	15
150-300	Hard	Nil	Nil
>300	Very Hard	Nil	Nil
%Na	Water classification	PRM	POM
<20	Excellent	2	1
<21	Good	18	29
<22	Permissible	15	17
<23	Doubtful	19	6
EC (µS/cm)	Water classification	PRM	POM
<250	Excellent	Nil	Nil
<250-750	Good	1	2
750-2000	Permissible	45	37
2000-3000	Doubtful	8	21
RSC	Water classification	PRM	POM
<1.25	Good	48	47
1.25-2.5	Doubtful	2	3
>2.5	Unsuitable	4	4

balanced alkalinity was calculated by $[Na] + [K] + [Ca] + [Mg] - [Cl] - [NO_3] - [SO_4]$ in mmol (Reuss and Johnson, 1986). The analytical precision for the measurements of ions was determined by the ionic balances, calculated as $100 \times (\text{cations} - \text{anions}) / (\text{cations} + \text{anions})$, which varies by about 5-10% and in few sites it exceeds 20% to 30%.

RESULTS AND DISCUSSIONS

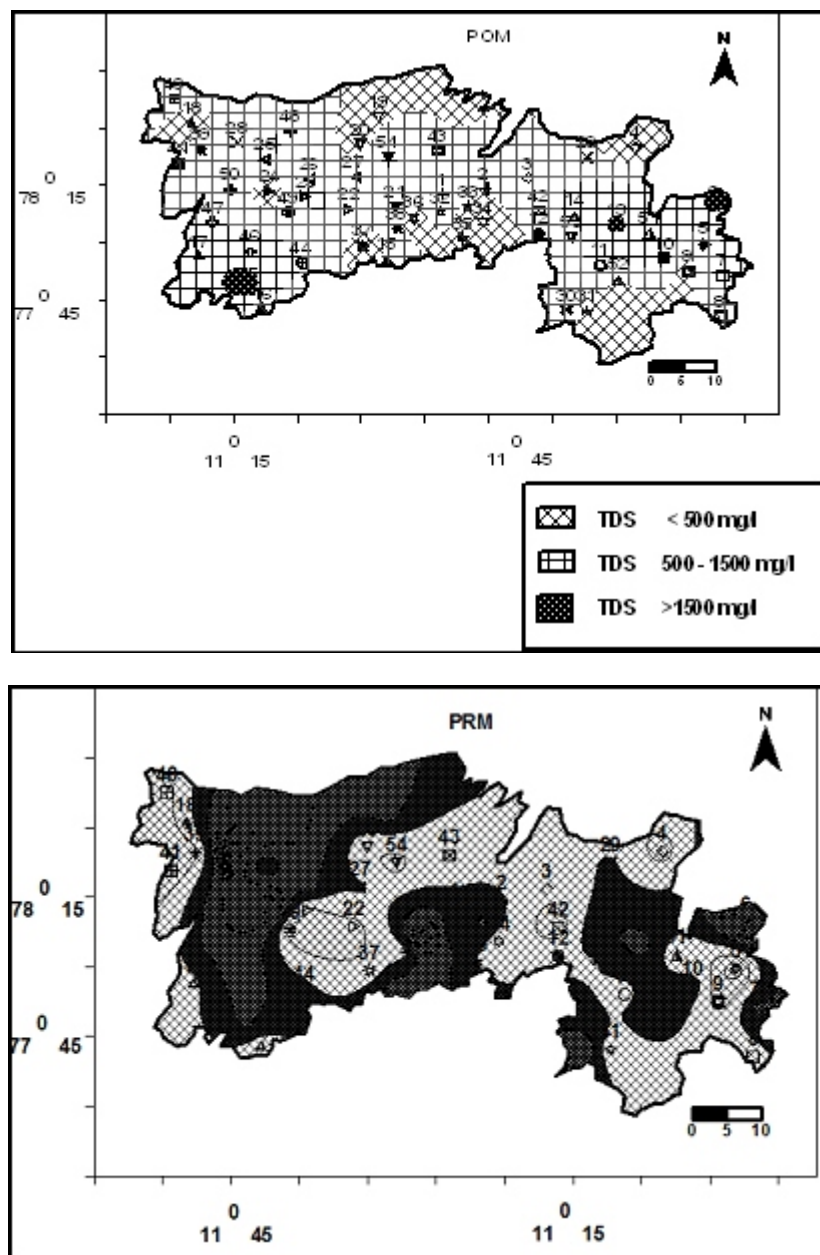
Hydrogeochemistry: The statistical parameters such as maximum, minimum, mean and standard deviation of different chemical compositions of groundwater samples are shown in the Table 1. Hydrogen ion was ranging from 7.0 to 9.0, EC from 221 to 3,800 µS/cm, HCO₃ from 5.0 to 979 mg/l, Cl from 31 to 975 mg/l, SO₄ from 1 to 184 mg/l, PO₄ from 0.01 to 5 mg/l, NO₃ from 1 to 162 mg/l, F from 0.1 to 3.0 mg/l, Si from 3 to 52 mg/l with an average of 8.0, 1790, 415, 357, 93, 1.0, 39.2 and 26 mg/l respectively. Ca, Mg, Na and K is ranging from 3 to 205,

21 to 484, 33 to 834, 0.2 to 384 mg/l with average of 94, 67, 175 and 13 mg/l respectively. The Box plot (Fig. 2) indicates the concentration distribution of the various major ions in the groundwater and shows that the hydrochemistry is dominated by pH, conductivity, TDS along with bicarbonates, calcium, magnesium and sodium ions irrespective of seasons. The abundance of major ions is in the order of $Na > Ca > Mg > K = Cl > HCO_3 > SO_4 > NO_3$.

Hydrogeochemical facies: The evolution of hydrochemical parameters of groundwater can be understood by plotting the concentration of major cations and anions in the Piper, 1944 diagram (Fig. 3). It helps in recognizing various hydrogeochemical types in a groundwater environment. The plot shows that most of the groundwater samples analyzed during both the seasons fall in the field of mixed Ca-Mg-Cl, Na-Cl, and Ca-HCO₃ type with minor representations from mixed Ca-Na-HCO₃ and Ca-Cl type. From the plot, it is observed that alkalinity (Na and K) exceeds alkaline earth (Ca and Mg) and strong acids exceed weak acids, in general water chemistry of the study area is dominated by alkali and strong acids.

Groundwater quality and assessment:

Drinking and domestic purposes: Groundwater quality assessment was carried to determine its suitability in terms of domestic and agricultural purposes based on the ISI, (1995) and WHO, (1996) standards (Table 2). Portability of drinking water is mainly based on recommended permissible limits of certain parameters, when exceeds the permissible limit it lays unfit for human consumption. Parameters exceeding permissible limits were identified in most of the locations indicating higher ionic concentration. TDS in majority of the samples are within the permissible limits of WHO and ISI with few exceptions irrespective of seasons. In the Table 3 major of the samples fall in fresh water irrespective of seasons with few representation from brackish water. Spatial distribution of TDS values was demarcated on the basis of

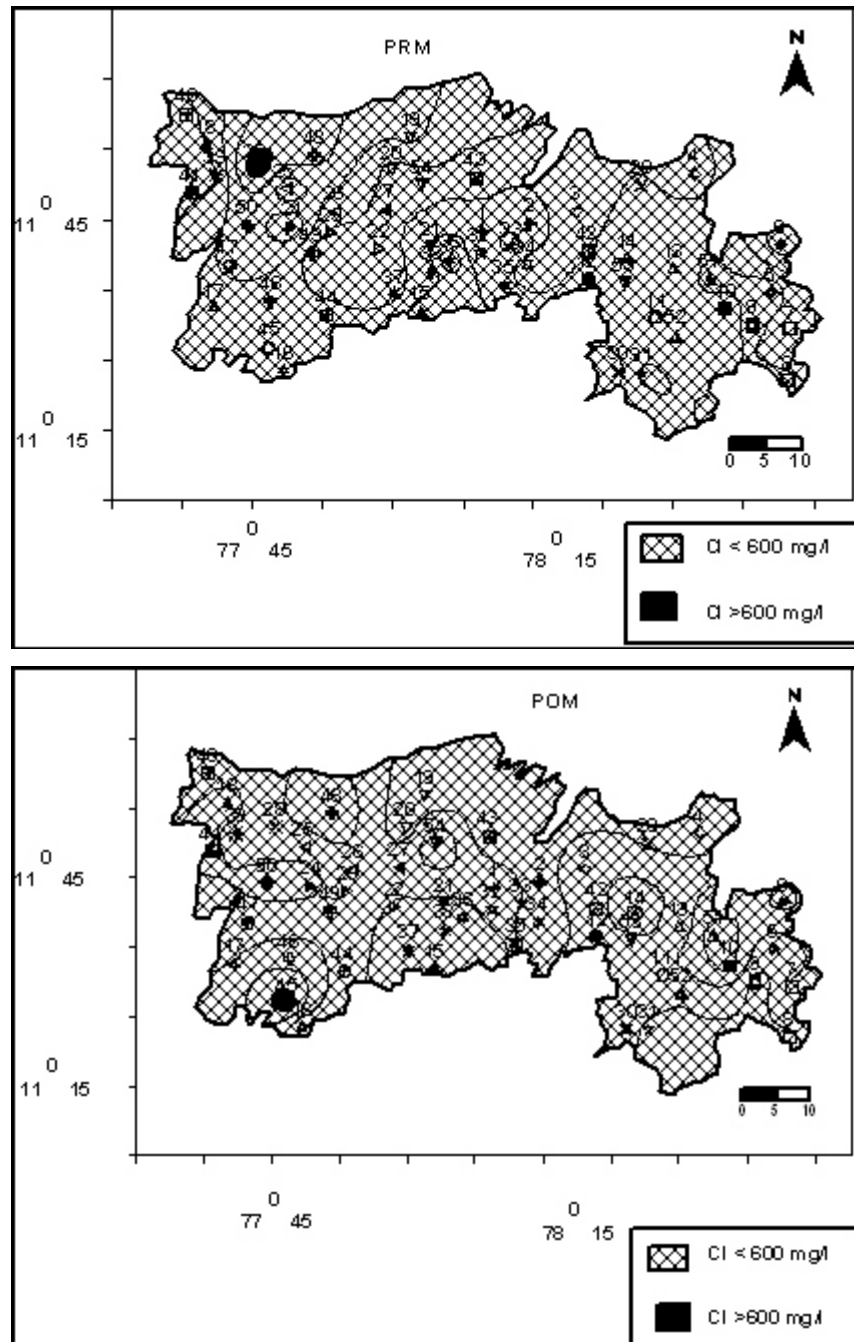


PRM - Pre monsoon season
 POM - Post monsoon season

Fig. 5: Spatial distribution of Cl from the study area

minimum and maximum permissible limit (<math>< 500 \text{ mg/l}</math>, $500-1500 \text{ mg/l}$ and $> 1500 \text{ mg/l}$) indicates majority of the study area is having higher TDS which cannot be used for safe drinking purpose (Fig.4). HCO_3^- is higher and exceeds ISI limit for drinking water indicating weathering from silicate and carbonate minerals chiefly calcite, plagioclase, gypsum and feldspars (Drever, 1997). The precipitation of CO_3 as scales in pipelines and affects pumps causing loss to farmers (Srinivasamoorthy *et al.*,

2008). Sodium was higher during both the seasons indicating their weathering from plagioclase bearing rocks. Potassium was lesser in both the seasons indicating its lower geochemical mobility. Calcium was well within the permissible limit irrespective of seasons. Magnesium was higher in PRM indicating the weathering from primary mineral sources. Hardness refers to reaction with soap and scale formation. It increases the boiling point of water and do not have any adverse effect on



PRM - Pre monsoon season
 POM - Post monsoon season

Fig. 6: Spatial distribution of NO_3 from the study area

human health. Hardness of the water varies from moderately hard to very hard (Table 3). Increasing of hardness was noted in both the seasons may be due to leaching of Ca and Mg ions into groundwater. Chloride exceeds the maximum limit in both the seasons, due to weathering from silicate rich rocks and leaching from soil due to infiltration from anthropogenic activities. Spatial

distribution of chloride was classified on the basis of maximum allowable limit of 600 mg/l (Fig. 5). Higher concentration >600 mg/l was confined to northeastern and northwestern part of the study area during PRM and POM. Since, due to the lack of Cl bearing minerals in silicate terrain, it might have derived from Anthropogenic (human) sources of chloride include fertilizer, road salt,

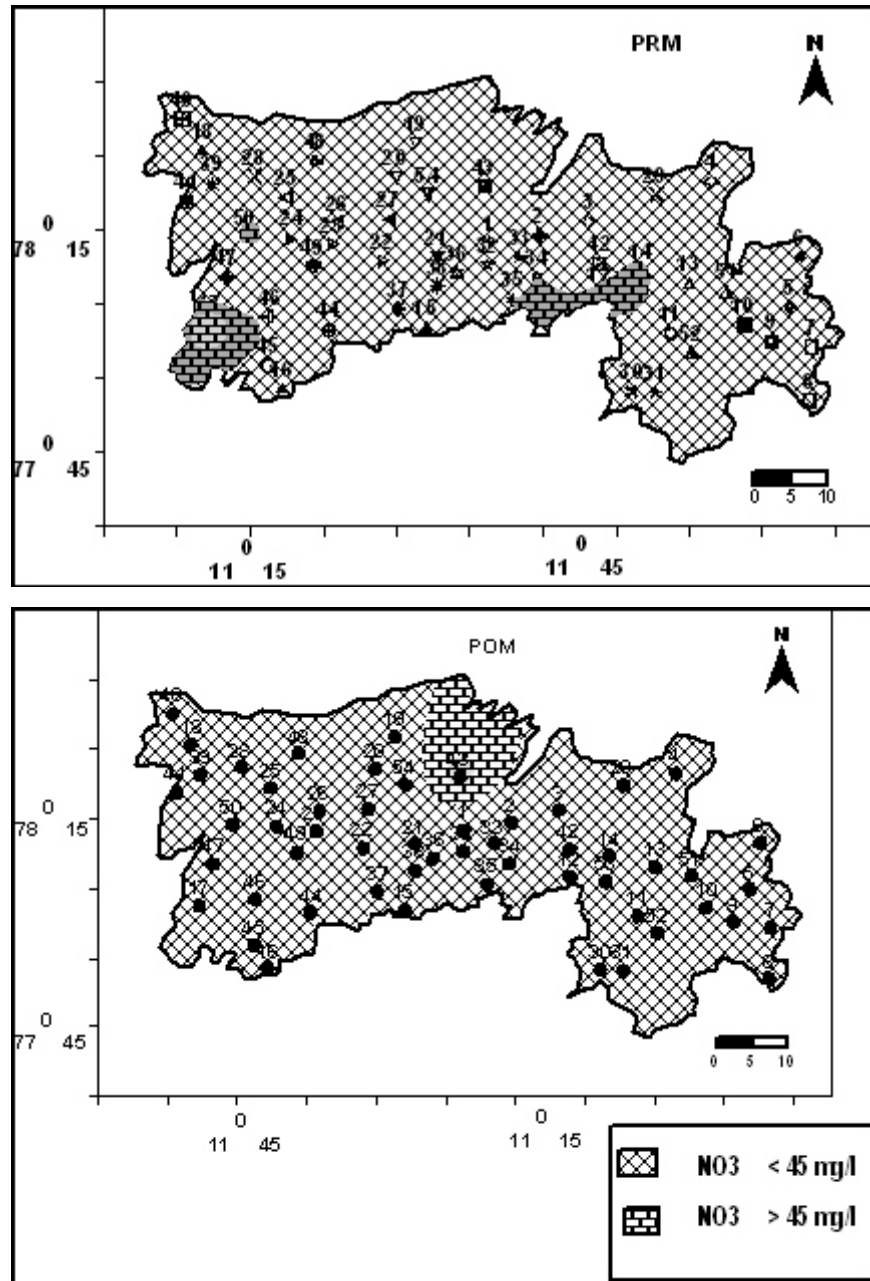


Fig. 7: Spatial distribution of PO_4 from the study area

human and animal waste, and industrial applications. These sources can result in significant concentrations of chloride in groundwater because chloride is readily transported through the soil (Stallard and Edmond, 1987). Nitrate is also exceeding the permissible limit of 45 mg/l. Higher concentration (>45 mg/l) was observed during PRM and lower (<45 mg/l) was observed during POM indicating dilution of groundwater with infiltrating rainwater (Fig. 6). Nitrogen in groundwater is mainly derived from organic industrial effluents, fertilizer or nitrogen fixing bacteria, leaching of animal dung, sewage

and septic tanks through soil and water matrix to groundwater (Richard, 1954). Phosphorus is not commonly toxic to humans, animals and fish, but creates taste and odour problems and difficulties in water treatment (Smeats and Amavis, 1981). The PO_4 was found to be higher than the prescribed limit of 0.54 mg/l in majority of samples during POM when compared with PRM. The spatial distribution of phosphate (Fig. 7) shows that during PRM all the samples were within the permissible limit but during POM cluster of high phosphates are confined to northern, northeastern and

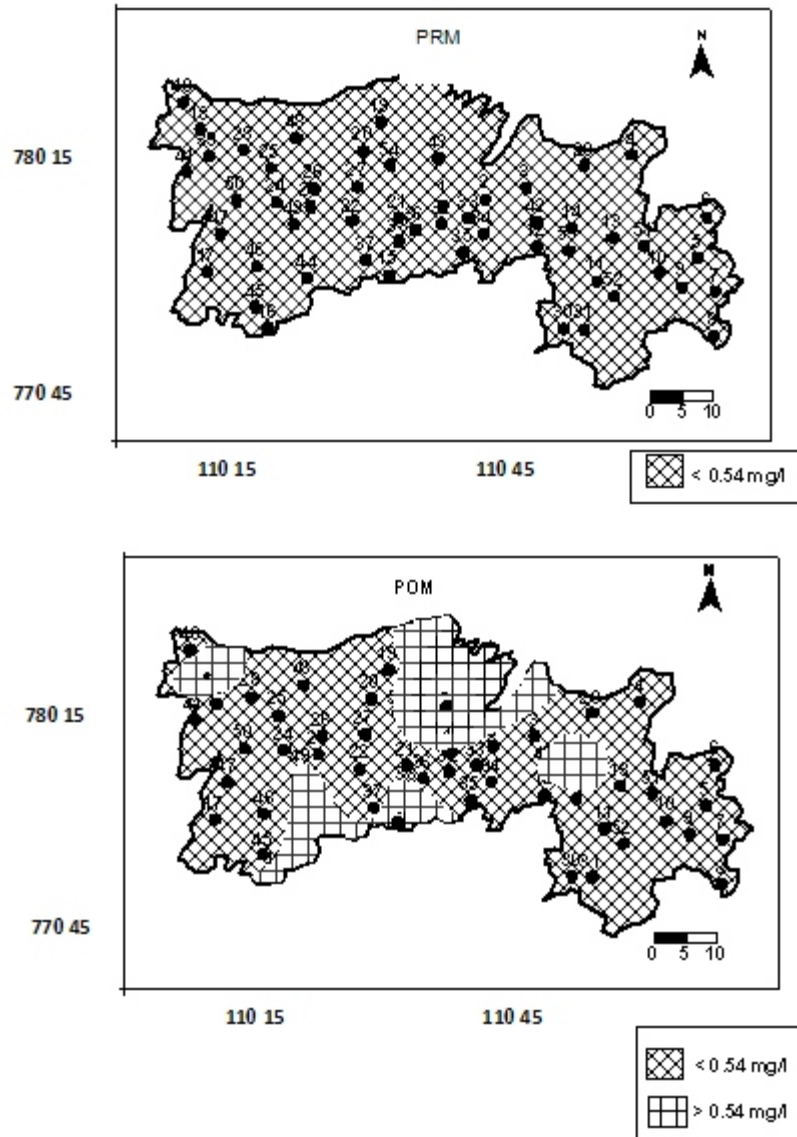


Fig. 8: Spatial distribution of F from the study area

northwestern part of the study area. Sulphate is found in smaller concentration due to its lesser breaking down of organic substances from weathered soil/water, leachable sulphate present in fertilizer and other human influences (Miller, 1979). Sulphate was within the permissible limit in both the seasons. Slight concentration (at least 0.5 mg/l) of fluoride in drinking water is beneficial, since it can help prevent dental caries. However, chronic ingestion of concentrations much greater than the WHO guideline value of 1.5 mg/l (WHO, 1984) may lead to dental fluorosis (tooth mottling), and in extreme cases skeletal fluorosis (bone deformation and painful brittle joints in older people) Hem, 1985; Appelo and Postma, 2005 and Apambire *et al.* 1997 summarized the likely impacts from long term consumption of fluoride bearing water. Higher concentration was noted during PRM due

to weathering and leaching of fluoride bearing minerals like apatite, biotite, muscovite, lepidolite and hornblende from the lithological units of the study area (Srinivasamoorthy *et al.*, 2008). Fig. 8 shows the spatial distribution of fluoride. Higher concentration was noted during PRM along northern part of the study area precisely surrounded by peninsular gneiss and charnockites.

Irrigation Purposes: Features that generally need to be considered for evaluation of the suitability of groundwater for irrigation use are Na%, SAR, and RSC. Sodium percentage values reflects water under the category of good (20–40 Na %), permissible (40–60 Na %) and doubtful (60–80 Na %). The values of sodium percent are varying from 19.75% to 66.57% (Table 3). Sampling

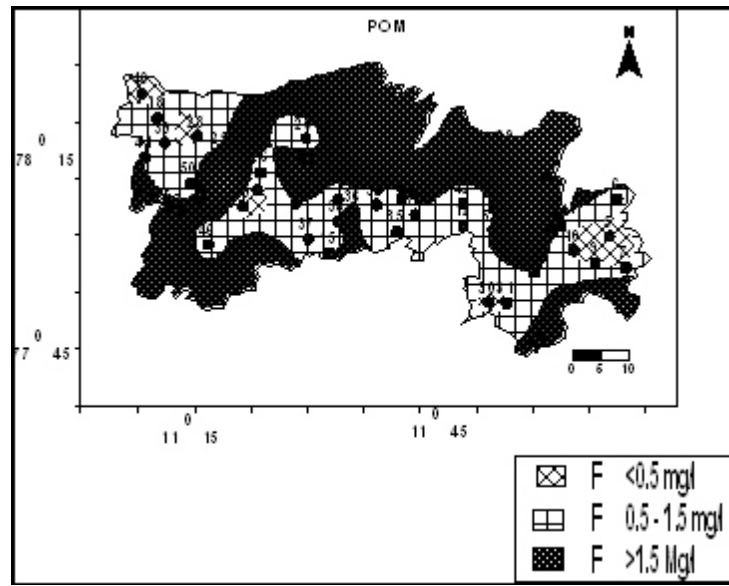


Fig. 9: Wilcox classification of groundwater in the study area

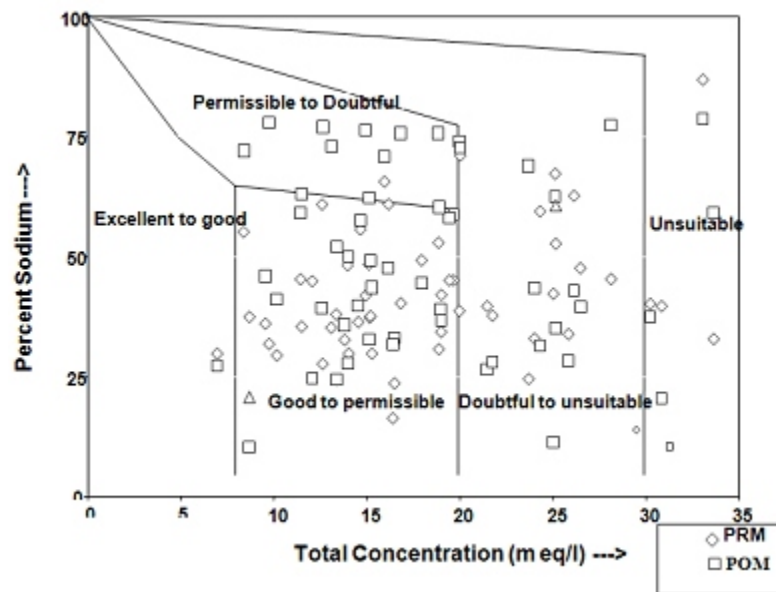


Fig. 10: USSL classification of groundwater in the study area

stations falling under the permissible category (83% and 69%), doubtful category (14% and 39%), good category (1% and 2%) during PRM and POM respectively with no representation in excellent category (Table 3) indicating their suitability for irrigation purposes. When the concentration of sodium ion is high in irrigation water, Na tends to be absorbed by clay particles, displacing magnesium and calcium ions. This exchange process of sodium in water for Ca and Mg in soil reduces the permeability and eventually results in soil with poor internal drainage. A perusal of (Wilcox, 1955) diagram

(Fig. 9) shows that six samples irrespective of seasons represents excellent to good, twenty samples in good to permissible , 15 samples in permissible to doubtful and all other samples in doubtful to unsuitable zones. Sodium concentration plays an important role in evaluating the groundwater quality for irrigation because sodium causes an increase in the hardness of the soil as well as a reduction in its permeability (Tijani, 1994). The sodium/alkali hazard is typically expressed as the SAR. This index quantifies the proportion of sodium (Na) to calcium (Ca) and magnesium (Mg) ions in a sample.

Sodium hazard of irrigation water can be well understood by knowing SAR which determines its utility for agricultural purposes. The analytical data plot on the US salinity diagram (USSL, 1954) plot (Fig. 10) illustrates that most of the groundwater samples fall in C3S1 zone during both PRM and POM indicating high salinity and low sodium water which can be used for irrigation for plants having moderate salt tolerance on soils. Soil in this terrain is preferable for salt tolerance plants. In water having high concentration of bicarbonate there is tendency for calcium and magnesium to precipitate as carbonates. To qualify this effect an experimental parameter termed as RSC (Eaton, 1950) was used. RSC is mainly due to increasing bicarbonate which precipitates calcium and magnesium as a result increases sodium in the form of sodium carbonate. Majority of samples irrespective of seasons fall in "good" zone of RSC (Richard, 1954) classification, (Table 3) indicating water is fit for irrigation purposes. Few representation of "medium" and "bad" water was also noted.

Industrial purpose: The quality requirements for industrial water supplies range widely and almost every industrial unit has its own standards. Water used by industry can be classified as cooling, boiler and process waters. Industries frequently suffer from incrustation and corrosion, which are chemical reactions caused by poor quality of waters. Incrustation involves deposition of undesirable material, whereas corrosion is a chemical action on metals, resulting in the metal being eaten away. In the present study, the following water quality criteria have been adopted (Subba *et al.*, 2005) for defining the incrusting and corrosive properties of waters: a Waters, having more than 300 mg/l of TH or 100 mg/l of SO₄ or 400 mg/l of HCO₃ or 40 mg/l of Si, may cause incrustation and water with pH less than 7 or TDS more than 1000 mg/l or Cl more than 500 mg/l may cause corrosion. The TH more than 300 mg/l is not represented in both the seasons whereas HCO₃ is more than 400 mg/l in both the seasons (Table 1), which may cause incrustation. The concentrations of SO₄ is more than 100 mg/l during both the seasons and Si is more than 40 mg/l during PRM indicating their ability to produce incrustation. The pH is in the range of 7.3– 8.1, and should not develop any corrosion. Higher concentration of TDS (>1,000 mg/l) in majority of the samples during both the seasons and higher content of Cl (>500 mg/l) in both the seasons may develop corrosion on metallic pipes and structures. As a whole, both these chemical reactions (incrustation and corrosion) can create adverse effects on processing, steaming and cooling, units if such waters are used by the industrial sectors.

CONCLUSION

Interpretation of hydrogeochemistry data reveals that groundwater in the study area is dominated by pH,

conductivity, TDS, bicarbonates, calcium, magnesium and sodium ions irrespective of seasons. The hydrochemical evolution plot indicates alkalinity exceeds alkaline earth and strong acids exceed weak acids. TDS, Ca and Si in majority of the samples are within the permissible limits of WHO and ISI with few exceptions irrespective of seasons., Na, K, Mg, Cl, F, SO₄, PO₄, HCO₃ and NO₃ are higher and exceeds the prescribed limit irrespective of seasons indicating the influence of weathering and anthropogenic impact. TH was higher in both the seasons due to leaching of Ca and Mg ions into groundwater. Spatial distribution of chloride indicates higher concentrations >600 mg/l are confined to northeastern and northwestern part of the study area. NO₃ exceeds the permissible limit of 45 mg/l indicating leaching from fertilizers during PRM. Phosphate was well within the permissible limit during both the seasons. Sulphate was within the permissible limit throughout the seasons. Higher fluoride was noted during PRM along northern part of the study area. Na% indicates majority of samples during both the seasons fall in permissible category. Wilcox diagram indicates majority of the samples represent in good to doubtful zone during both the seasons. The US salinity diagram indicates that high salinity and low sodium water can be used for irrigation for plants having moderate salt tolerance on soils. RSC in majority of samples fall in good category indicating the water fit for irrigation purposes. The TH, TDS, SO₄, HCO₃ and Si values are noted to be higher indicating the quality of water if used will result in incrustation and corrosion of pipes.

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