Hydrogeochemistry and groundwater quality assessment of Ranipet industrial area, Tamil Nadu, India

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One of the highly polluted areas in India located at Ranipet occupies around 200 tanneries and other small scale chemical industries. Partially treated industrial effluents combined with sewage and other wastes discharged on the surface cause severe groundwater pollution in the industrial belt. This poses a problem of supply of safe drinking water in the rural parts of the country. A study was carried out to assess the groundwater pollution and identify major variables affecting the groundwater quality in Ranipet industrial area. Twenty five wells were monitored during pre- and post-monsoon in 2008 and analyzed for the major physico-chemical variables. The water quality variables such as total dissolved solids (TDS), Iron (Fe^{2+}), Hexavalent Chromium (Cr^{6+}), at most of the sampling locations exceeded the ISI and WHO guideline levels for drinking water. Multivariate statistical techniques such as factor analysis were applied to identify the major factors (variables) corresponding to the different source of variation in groundwater quality. The water quality of groundwater is influenced by both anthropogenic and chemical weathering. The most serious pollution threat to groundwater is from TDS, Cr^{6+} and Fe^{2+} , which are associated with sewage and pollution of tannery waste. The study reveals that the groundwater quality changed due to anthropogenic and natural influences such as agricultural, natural weathering process.

1. Introduction

Rapid growth of urban population, development of agriculture and industrial activities especially in hard rock terrains caused an intense increase in water consumption. Overexploitation together with a decrease in precipitation and water table decline are the most serious problems for the quality of groundwater in urban areas with highly dense population. Particularly, the process of tanning involves the use of large amounts of water and various chemicals like lime, sodium-carbonate, sodium-bi-carbonate, common salt, sodium-sulphate and chrome-sulphate. It is established that a single tannery can cause the pollution of groundwater around the radius of 7–8 km (CLRI 1990; Ansari

et al. 1999). Chromium present in effluent is primarily in the less toxic trivalent form (Cr^{3+}) but when this effluent is discharged into the soil, due to varying environmental conditions, Cr^{3+} is oxidized to toxic hexavalent form, which seldom remains as Cr^{6+} (Anderson 1999; Selvakumar and Manoharan 2002; Srinivasa Gowd *et al.* 2005; Thangarajan *et al.* 1999; Mondal and Singh 2005). Several authors have reported about the presence of contaminants in soils (Wu 1980) and waters (Kolpin *et al.* 1998) in various part of the globe and also in India (Srinivasa Rao *et al.* 1997; Elango *et al.* 2003). Contamination of the groundwater by domestic, industrial effluents and agricultural activity is a serious problem faced by developing countries.

Keywords. Hydrochemistry; quality analysis; factor analysis; groundwater quality assessment.

The conventional methods (histograms, trilinear, semi-logarithmic) deal with a limited number of variables that are responsible for the groundwater chemistry (Matthess 1982; Hem 1989). Multivariate analyses, such as cluster and factor analyses, are used to incorporate larger number of variables measured in groundwater systems. Factor analysis is used simply as a numerical method of discovering variables that are more important than other data for representing parameter variation or demonstrating hydrochemical processes. The basic

purpose of factor analysis is to study the hydro-geochemistry of an aquifer and explain a large amount of the variance of the analytical data by a small number of factors (Ruiz *et al.* 1990). Factor analysis has been successfully applied to clarify the contributing hydrogeological and hydrogeochemical processes that result in the quality of water observed during aquifer monitoring (Usunoff and Guzman 1989; Razack and Dazy 1990; Briz-Kishore and Murali 1992; Suk and Lee 1999). In the present context of study, particular emphasis is

Figure 1. Location of observation wells and geology map of the study area.

placed on the status of groundwater pollution due to the effluents of chemical manufacturing industries and tannery industries in the study area. To keep this view in mind that textile and tannery industries are the major source of pollution and contributors of metals to the environment, a systematic study was required to ascertain the status of chemical constituents and metals in textile and tannery effluents and associated groundwater. Therefore, this study aimed to assess the current state of water quality and identify the major factors affecting on water quality of groundwater in the Ranipet industrial area.

2. Study area

The study area is located in 79°26'45"–79°37'69"E longitude and 12°92'25"–12°98'87"N latitude and the watershed covering the study area spread over 54 km² (figure 1). It is one of the biggest exporting centers of tanned leather in India and discharging their effluents on the open land and surrounding water bodies (Govil *et al.* 2004). All tannery industries located in Ranipet are discharging effluents into Puliankannu, Karai, Puliathengal, Vanapadi, and Thandalam lakes and it is a matter of increasing concern, as these industries are located in Palar River Basin.

3. Geology and geohydrology

The study area predicts undulating topography, falling in pediment zone and structural hills in the northern side. The flat to undulating pediplain nature continue and extends up to the flood plain of Palar River. The pediplain has granites, gneisses and basic and ultra basic intrusive, which are discontinuous unconfined to semi-confined aquifers down to 150 m bgl and restricted to weathered zone and fractures GSI (2000). The major dolerite dyke, striking NE–SW passes through the factory area (Sankaran *et al.* 2009). Quaternary sediments are restricted to the alluvial sand and clay of the Palar River and its tributaries. Sand thickness in the Palar River is hardly 10 m and the width being 2000 m along the river course (Rao *et al.* 2009). The alluvium consisting of fine to coarse sand and clay occurring in the area is of a fluvial origin and restricted to the course of Palar River and major streams (Subramanian and Selvan 2001). Discontinuous unconfined to semi-confined aquifers down to 150 m bgl restricted to weathered zone and fracture zone have been encountered in the granite and gneissic formations in the Palar basin (figure 1).

4. Materials and methods

A total of 25 representative groundwater samples were collected for two different seasons, viz., pre-monsoon (June) and the post-monsoon (December) along with a maximum representation covering the entire study area (figure 1). Groundwater samples were collected in 1000 ml polythene bottles pre-cleaned with double distilled water. The collected samples were filtered by Whatman filter paper prior to their analysis in the laboratory. The samples were analyzed for all major ions by following standard methods (APHA 1998) including Hexavalent chromium (Cr⁶⁺) for both pre- and post-monsoon during 2008 (figure 1). pH, TDS and EC were measured by water quality analyzer (Systronics Model 371). SO₄^{2−} was determined by digital spectrophotometer model GSS 700A (Electronic Corporation of India). Ca²⁺ and Mg²⁺ were analyzed by EDTA titration. Chloride (Cl[−]) was determined by ion selective electrode method (Cole-Parmer iodine electrode, model no. 27502-13). Bicarbonate (HCO₃[−]) concentrations of the groundwater were determined by potentiometric titration method. SO₄^{2−} was determined by digital spectrophotometer model GSS 700A (Electronic Corporation of India). Nitrate (NO₃[−]) was measured by using ion selective electrode method (Cole-Parmer iodine electrode, model no. 27502-19). Total hardness (TH) of the groundwater was calculated using the formula given by Sawyer *et al.* (2003):

$$\text{TH (as CaCO}_3\text{) mg/L} = (\text{Ca}^{2+} + \text{Mg}^{2+}) \times 50$$

where the concentrations of Ca²⁺ and Mg²⁺ are represented in meq/l.

The Cr⁺⁶ and Fe²⁺ concentrations in samples were determined colorimetrically by using spectrophotometer at 540 nm by diphenyl carbazide (DPC) method (APHA 1998).

Factor analysis and derivative methods have been widely used in geochemical applications to identify pollution sources and to apportion natural *vs.* human contributions (Chen *et al.* 2005). Factor analysis is a multivariate technique designed to analyse the interrelationships within a set of variables. The factors are chosen in such a way that it reduces the overall complexity of the data by taking advantages of inherent interdependencies (Davis 2002). To undertake factor analysis (FA), the SPSS (predictive analytics software) factor analysis module (Field 2005) was used, specifying the principal component method with varimax rotation (Kaiser 1958). In order to determine a number of factors the Kaiser criterion was applied (Chen *et al.* 2005). The rotation of the components axis is performed so that components are clearly defined by high

loadings for some variables and low loadings for others, facilitating the interpretation in terms of original variables. FA is also used as a classification technique, useful for hydrochemical facies investigation and interpretation of their origin (Lawrence and Upchurch 1983). FA can be applied to investigation of groundwater contamination (Subbarao *et al.* 1995; Grande *et al.* 1996; Jeong 2001). This study area was evidence of groundwater chemistry transformations due to anthropogenic contamination. This situation is connected mainly to shallow unconfined aquifers but increasingly contamination appears in deep aquifers, covered by complex of geological features in the study area. The investigation of groundwater contamination is complicated (particularly in cases of early phase groundwater contamination) because of changes in groundwater chemistry caused by contamination and natural (geogenic) hydrogeochemical processes overlap.

5. Results and discussion

5.1 Chemistry of groundwater

Water quality analysis has been carried out for major ions and Hexavalent chromium (Cr^{6+}) and Iron (Fe^{2+}) of groundwater samples and the analytical results of the chemical analysis and the statistical parameters such as minimum, maximum, mean are presented in table 1 for both pre-monsoon and post-monsoon. And also plotted spatial variations of different constituents in figure 2(a–g). The pH of groundwater ranges from 6.65–11.49 and 6.62–11.68 for both seasons. High pH in groundwater indicates that it is alkaline in nature. Significantly elevated concentration of pH observed in R1 and R5 inside TCCL is due to the anaerobic conditions (figure 2a). The total dissolved solids (TDS) in groundwater ranges from 174–4522 mg/l and 94–1854 mg/l in both pre- and post-monsoon. TDS concentration of groundwater has been found slightly reduced during post-monsoon (figure 2b). The electrical conductivity (EC) in groundwater varies from 272–5520 $\mu\text{S}/\text{cm}$ and 268–4100 $\mu\text{S}/\text{cm}$ in both pre- and post-monsoon (figure 2c). The elevated concentration of TDS and EC was resulted from domestic sewage water in the Pulianthangal village (R15) and agriculture contamination in the well (R28 and R9) near Palar River in pre-monsoon. There is a considerable amount of dilution of concentration of ions during the post-monsoon due to precipitation (Rao *et al.* 2011). As per the TDS classification (Fetter 1990), most of the groundwater samples collected during the pre-monsoon and post-monsoon periods belong to brackish type ($\text{TDS} > 1000 \text{ mg/l}$). The groundwater classifications of Freeze and Cherry (1979) and

Table 1. Drinking water specification given by WHO (1984) – minimum, maximum and average ion concentration.

Water quality parameter	WHO limits		Quality status in the study area					
	Maximum acceptable limit (mg/l)	Maximum allowable limit (mg/l)	Pre-monsoon			Post-monsoon		
			Min (mg/l)	Max (mg/l)	Mean (mg/l)	Min (mg/l)	Max (mg/l)	Mean (mg/l)
EC	–	–	272	5520	2301	268	4100	2005.2
TDS	500	1500	174	4552	1514	94	1854	853.24
pH	6.5	8.5	6.65	11.49	7.63	6.62	11.68	7.55
Potassium	–	12	0.26	46	15.06	0.8	17.1	5.8
Sodium	–	200	20	1010	341	16	54.1	840
Chloride	200	600	14	1537	321	22	749	225
Sulphate	200	400	8	1605	456	23	855	227.44
NO_3 as Nitrate	12	–	0.21	36.8	6.2	0.06	51.2	10
Iron	0.3	1	0.04	11	0.93	0.02	0.41	0.1
Hex-Chromium	0.05	0.05	0.02	220.33	35.2	0.01	275	36.4

Figure 2. Spatial variation of (a) pH, (b) TDS (mg/l), (c) EC ($\mu\text{S}/\text{cm}$), (d) Cl (mg/l), (e) SO_4 (mg/l), (f) $\text{NO}_3\text{-N}$ (mg/l), (g) K (mg/l), (h) Na (mg/l) and (i) Fe^{+2} (mg/l) for pre-monsoon and post-monsoon.

Davis and DeWiest (1966) are presented in tables 2 and 3.

The chloride (Cl^-) concentration in groundwater ranges from 14–1537 mg/l and 22–749 mg/l in both pre- and post-monsoon. The Cl^- concentration also has shown elevated ranges in groundwater during pre-monsoon as compared those of post-monsoon (figure 2d). The elevated concentration of Cl^- is seen in the VOC Nagar at well no.

R23 in pre-monsoon. The sulphate (SO_4) concentration in groundwater ranges from 8–1605 mg/l and 23–855 mg/l in both seasons. SO_4^{2-} concentrations were elevated during pre-monsoon (figure 2e). The pre-monsoon SO_4^{2-} concentration are reported in well nos. R4 (1605 mg/l), R6 (666 mg/l), R7 (579 mg/l) and R20 (687 mg/l). In post-monsoon season only one well R7 (729 mg/l) is showing high concentration. Elevated SO_4^{2-} concentration

Figure 2. (Continued)

of 1605 mg/l in groundwater has been reported in well no. R4 inside TCCL. It is possible that the waste sludge in the dump may be contributing as chromium sulphate. Outside the TCCL premises, the well R6, near MGR Nagar, has also reported elevated SO_4^{2-} concentrations of 666 and 725 mg/l, respectively for pre- and post-monsoon. The pre-monsoon SO_4^{2-} concentration in well R20 (687 mg/l), located in the premises of SIPCOT Ltd (in an industrial area) has indicated the severe

nature of groundwater contamination. Significantly there is no nitrate contamination reported in the groundwater samples except R23 (36.8 mg/l) and R24 (14.2 mg/l) for pre-monsoon and R13 (18.8 mg/l), R20 (15.8 mg/l), R24 (51.2 mg/l), and R25 (16.18 mg/l) in VOC Nagar for post-monsoon, due to the anthropogenic (domestic/sewage) activities (figure 2f). The potassium (K^+) concentrations are varying from 0.26–46 mg/l and 0.8–17.1 mg/l for both pre- and post-monsoon. Elevated K^+

Figure 2. (Continued)

Table 2. Groundwater classification (Davis and DeWiest 1966).

TDS (mg/l)	Water quality	Pre-monsoon	Post-monsoon
Up to 500	Desirable for drinking	174–497(2)	94–346(4)
500–1000	Permissible for drinking	523–905(6)	570–980(15)
Up to 3000	Useful for irrigation	1025–2752(13)	1020–1854(6)
Above 3000	Unfit for drinking and irrigation	3366–4522(3)	

concentrations are observed in pre-monsoon season at R15 (Pulianthangal village), R23 (VOC Nagar) and R29 (Near Palar River) (figure 2g).

The sodium (Na^+) concentrations in groundwater ranges from 20–1010 mg/l and 16–54.1 mg/l in both seasons (figure 2h). Na^+ was higher in

Table 3. Groundwater classification (Freeze and Cherry 1979).

TDS (mg/l)	Water quality	Post-monsoon	Pre-monsoon
0–1000	Freshwater	174–905(8)	94–980(19)
1000–10,000	Brackish water	1025–4522(16)	1020–1854(6)
10,000–100,000	Salty water		
> 100,000	Brine

Figure 3. Spatial variation of Cr^{+6} (mg/l) for pre-monsoon and post-monsoon.

pre-monsoon season indicating weathering from plagioclase bearing rocks (Srinivasamoorthy *et al.* 2008; Rao *et al.* 2011). High concentration of Na^+ was predicted in the R15 (Pulianthangal village), R23 (VOC Nagar) and R29 (Near Palar River).

5.2 Metal concentrations

In the case of iron, the concentration of Fe^{2+} in many of the stations is higher than the WHO (1984) permitted limit of 0.3 mg/l. The concentration of Fe^{2+} varying from 0.04–11.0 and 0.02–0.41 mg/l for both pre- and post-monsoon (figure 3a). Elevated values of iron concentrations were observed at R1 (1.36 mg/l), R6 (1.31 mg/l), R10 (0.44 mg/l), R13 (0.6 mg/l), R15 (0.84 mg/l), R22 (11.0 mg/l), R24 (4.13 mg/l) and R25 (0.45 mg/l), in pre-monsoon. There is a significant elevated concentration observed in the downstream of TCCL (R22) and Maniyampettai colony (R24) in pre-monsoon season.

Chromium occurs in higher concentrations in the wastes from electroplating, paints, dyes, chrome tanning, paper industries, etc. Maximum contaminant level of chromium for the drinking water is 0.05 mg/l (WHO 1984). The hexavalent chromium (Cr^{6+}) concentrations are varying from 0.02 to 220 mg/l and 0.01 to 275 mg/l

during both pre- and post-monsoon (figure 3b). The wells R1 (103.4–109 mg/l), R2 (69.85–64 mg/l), R3 (38.58–53 mg/l), R4 (220.33–185 mg/l), R5 (95.6–275 mg/l), R6 (160.9–225 mg/l), R7 (0.9–0.01 mg/l), R18 (3.48–BDL mg/l) in both pre- and post-monsoon. Elevated Cr^{6+} concentrations were observed in both seasons, due to the chromium dump inside TCCL which is contaminating the downstream area (Rao *et al.* 2009). The wells R1–R5 are located within the TCCL industrial premise and are highly contaminated with Cr^{6+} and downstream of R18. High concentration of Cr^{6+} observed in the Anna Nagar (R26) upstream of the TCCL area due to the leather industrial activities.

5.3 Groundwater quality and assessment

Groundwater quality assessment of the study area was carried out to determine its suitability in terms of domestic and agricultural purposes based on the WHO (1984) standards (table 1). The quality of groundwater in the study area is highly influenced by anthropogenic contamination. R1, R2, R3, R4 and R5 samples inside in TCCL premises, 18 near adjacent to TCCL, R6 and R7 in MGR Nagar, R15 in Pulianthangam village, R20 and R21 in SIP-COT industrial area, R23 in VOC Nagar and R24 and R25 in Maniyampettai colony in pre-monsoon

and post-monsoon seasons exceed TDS concentration recommended by WHO (1984) and ISI (1983). The sodium concentrations exceeded in some locations like R1, R2, R3, R4 and R5 samples inside in TCCL premises, R18 adjacent to TCCL and R7 in MGR Nagar in both seasons due to the sodium salts used in TCCL industry (Rao *et al.* 2009, 2011). The potassium concentration exceed in pre-monsoon recommended by WHO (1984) in and around TCCL area only. The chloride concentrations in MGR Nagar, VOC Nagar, SIPCOT industrial area and Anna Nagar (R26) were shown elevated values due to leaching migration from upper soil layers due to industrial and domestic activities and dry climates (Srinivasamoorthy *et al.* 2008). Nitrate as N concentrations are observed in R20 and R21 in pre-monsoon and 13 (VOC Nagar), R20, R24 and R25 in post-monsoon seasons. High nitrate concentrations in groundwater could pose potential hazard to infant health. The consumption of water with high nitrate concentration decreases the oxygen-carrying capacity of blood, causing blue babies or methemoglobinemia (Jeevanandam *et al.* 2006). High SO_4^{2-} concentration were observed in TCCL (R4), MGR Nagar (R6) and SIPCOT (R20) in pre-monsoon and R7 near MGR Nagar in post-monsoon; it could be possible that the waste sludge in the TCCL (chromium dump) may be contributing chromium sulphate and migrating towards downstream area (Rao *et al.* 2009).

The iron concentration in nine samples exceeds the maximum permissible limit of 0.3 mg/l as per WHO (1993) standards in TCCL, VOC Nagar, SIPCOT industrial area, Maniyampettai colony and Pulianthangam village. Higher iron content may produce undesirable effects such as astringent taste, discoloration, turbidity, deposits, and growth of iron bacteria in pipes affecting the acceptability of water for domestic use (Das and Borah 1983). The shortage of iron causes a disease called 'anemia' and prolonged consumption of drinking water with high concentration of iron may lead to liver disease called as 'haemosiderosis' (Rajgopal 1984).

The chromium (Cr^{6+}) concentration in six samples in and around TCCL and 2 samples in MGR Nagar exceeds the maximum permissible limit of 0.05 mg/l as per WHO (1993) standards. The study area predominantly composed of granite rocks, where chromium concentration is always below 50 mg/kg, it is not possible to derive such high levels of Cr from rocks (Fendorf 1995; Edmunds and Smedley 1996). Therefore, the source of Cr appears to be anthropogenic activity from the TCCL. Chromium is an essential trace element, required for the metabolism of lipids and proteins and to maintain a normal glucose tolerance factor. High doses of chromium cause liver and kidney damage and chromium dust is carcinogenic

(SEGH 2001). Chromium can cause allergic reactions in the skin, damage the lungs, and asthma attacks (ATSDR 2005). Chromium is water soluble and extremely irritating and toxic to human body tissue owing to its oxidizing potential and permeability of biological membranes (Anderson 1999).

5.4 Factor analysis

R-mode factor analysis was applied to obtain correlations among the hydrochemical constituents of groundwater samples (Brown 1998; Kouping *et al.* 2006), and all the chemical constituents were plotted (figure 4) for both pre- and post-monsoon. The aim is to evaluate the variables belonging to a specific chemical process and also to find out the dominance and contribution of the major elements in terms of the total dataset. Varimax rotation is a commonly employed method for assisting in factor identification, which was useful, in this application, to place the contaminants on a minimum number of factors. After several trial runs, it was found that extracted five factors in pre-monsoon and four factors in post-monsoon during the analysis and their loading, communalities for each variable, percentage of the variance of each factor, and cumulative percentage of variance are listed in tables 4 and 5. Liu *et al.* (2003) classified the factor loading as 'strong', 'moderate' and 'weak' corresponding to absolute loading values of >0.75 , $0.75-0.50$ and $0.50-0.40$, respectively. The factors, which best describe the variance of the analysed data (eigen value >1) and can be reasonably interpreted, were accepted for further analysis. The sum of squared factor loadings (communality) shows how the obtained factors describe variance of particular variables. Finally, factor scores were calculated for each sample. Extreme positive factor scores ($> +1$) reflect areas most affected, and negative (< -1) reflect areas unaffected by the chemical process represented by the factor. Near-zero scores reflect areas affected to an average degree of the process or factor.

FA of the pre-monsoon data rendered four significant (eigen value >1) factors explaining 85.9% of the total variance (table 4). Factor 1 explains 26.8% of the variance and has strong loadings of TA (0.816), Ca^{2+} (0.834) and Na^+ (0.939), whereas SO_4^{2-} (0.635) showing moderate loadings. The high loading of TA (>0.75) indicates that sources of major ionic constituents are the poor domestic sewerage system and the tanneries. Chloride ion has higher dominant leaching ion from upper soil layers due to industrial and domestic activities and dry climates (Srinivasamoorthy *et al.* 2008). Sodium ion in groundwater derives from the incongruent

Figure 4. Plot of factor loadings for the first two factors in pre-monsoon and post-monsoon.

Table 4. Factor analysis of groundwater samples in the study area – Pre-monsoon (June 2008).

Parameter	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Communalities
pH	0.166	-0.181	-0.802	0.144	0.261	0.792
EC	0.375	0.061	0.001	0.446	0.618	0.725
TA	0.816	0.001	-0.307	-0.227	0.21	0.855
Cl	0.834	-0.046	0.331	0.368	-0.121	0.957
SO ₄	0.635	-0.189	0.426	0.346	0.04	0.742
NO ₃ -N	-0.193	0.871	0.125	-0.113	-0.176	0.856
Na	0.939	-0.149	-0.044	0.184	0.016	0.94
K	0.143	-0.06	-0.05	0.966	-0.023	0.96
TH	0.272	-0.021	0.806	0.099	0.478	0.962
Fe ²⁺	-0.008	0.916	-0.004	0.03	0	0.84
Cr ⁶⁺	-0.11	-0.182	-0.02	-0.141	0.874	0.83
Eigen values	2.958	1.732	1.697	1.537	1.534	
% of variance	26.893	15.747	15.429	13.97	13.949	
Cumulative %	26.893	42.64	58.069	72.039	85.988	

dissolution of plagioclase in granite, chemical fertilizer, domestic effluents and atmospheric input (Aiuppa *et al.* 2003; Valdes *et al.* 2007). The loading of SO₄²⁻ is due to the chromium sulphates used in tannery industries (Rao *et al.* 2009; Bhardwaj *et al.* 2010). Factor 2 (tannery pollution factor) explains 15.7% of variance and has strong loadings of Nitrate as N (**0.871**) and Fe²⁺ (**0.916**). There was no known lithologic source for Nitrate as N, and generally atmospheric deposition was not considered to be a major source of Nitrate as N concentrations in the groundwater (Handa 1988), the substantial contribution of Nitrate as N in the study area was likely resulted from domestic sewage effluents and industrial inputs to groundwater. Factor 3 explains 15.4% of the variance and has strong negative loading of pH (-0.802) and strong positive loading (0.806) of TH. Factor 4 explains 13.9% of the variance and has strong positive loading of K (0.966). Potassium ion in groundwater

often comes from orthoclase and muscovite minerals present in granite, and from pollution sources such as domestic effluents. Factor 5 explains 13.9% of the variance and has strong positive loading of Cr⁶⁺ (0.874) and moderate loading of EC (0.618). Electrical conductivity of groundwater was largely influenced by factor 2; natural processes as well as anthropogenic inputs may determine its level. Electrical conductivity originates from the anthropogenic activities and Cr⁶⁺ originate from some common processes in the textile industry. The sources of these trace metals, especially chromium, are the tanneries located in the area.

FA of the post-monsoon data rendered that five factors accounted for 82.3% of the total variance (table 5). These factors with different factor loadings indicate that different contributions are involved in determining the chemical compositions of groundwater in the study area. Factor 1, accounting for about 29.01% of the variance

Table 5. *Factor analysis of groundwater samples in the study area – Post-monsoon (December 2008).*

Parameter	Factor 1	Factor 2	Factor 3	Factor 4	Communalities
pH	0.842	0.072	-0.396	-0.089	0.878
EC	0.452	0.784	0.389	0.089	0.979
TA	0.902	0.092	0.007	0.055	0.826
Cl	-0.311	0.825	0.14	0.332	0.907
SO ₄	0.268	0.127	0.854	-0.2	0.858
NO ₃ -N	-0.096	-0.046	0.044	0.906	0.834
Na	0.315	0.723	0.086	-0.12	0.644
K	0.009	0.693	0.036	-0.362	0.613
TH	-0.238	0.234	0.842	0.265	0.891
Fe ²⁺	0.626	0.172	0.373	-0.434	0.75
Cr ⁶⁺	0.862	0.041	0.296	-0.228	0.885
Eigen values	3.197	2.416	2.004	1.446	
% of variance	29.06	21.961	18.222	13.149	
Cumulative %	29.06	51.021	69.243	82.392	

and was primarily composed of pH (0.842), TA (0.902), Cr⁶⁺ (0.862) pH and Fe²⁺ (0.626). TA and Cr⁶⁺ constituents are showing strong positive loading (>0.75) and Fe²⁺ is showing weak loading (0.75–0.50). Factor 2, accounting for about 21.9% of the variance and was primarily composed of EC (0.784), Cl⁻ (0.825), Na⁺ (0.723) and K⁺ (0.692). EC, Na⁺ and Cl⁻ are showing high positive loading (>0.75) and K⁺ is showing moderate loading (0.75–0.50). Factor 3, accounting for about 18.2% of the variance and was primarily composed of SO₄²⁻ (0.854) and TH (0.842). Factor 4, accounting for about 13.1% of the variance and associated with very high loading of Nitrate as N (0.906).

Comparison of FA for the two seasons shows the effect of groundwater recharge caused by monsoon and it appears that the major ion pollution factor shows little change during the post-monsoon season, but there is considerable reduction in pollution load caused by the tannery pollution factor. This is evidenced by the substantial reduction in the concentration of trace metals notably Cr⁶⁺ and Fe²⁺, and major ionic constituents such as Na⁺, Cl⁻ and SO₄²⁻ during the post-monsoon season.

6. Conclusions

The hydrochemistry of the groundwater varies in relation to different anthropogenic activities, intrusion of polluted domestic sewage water, and seepage of tannery pollutants. The pre-monsoon values indicate that most of the groundwater belongs to the brackish type and it has been found that much

of dilution has occurred during the post-monsoon where the TDS values were significantly lowered. Moreover, the TDS values of the groundwater are higher than the permissible limit for both the pre- and post-monsoon samples. The nitrate and potassium concentrations of pre-monsoon groundwater samples are higher than the WHO, ISI permissible limits in certain places but got diluted in post-monsoon. The result of the trace metal concentrations shows that Fe²⁺ and Cr⁶⁺ are found to be higher than the prescribed limit. The factor analysis of the major ion chemistry of the groundwater reveals five in pre-monsoon and four in pre-monsoon prevalent factors operating in these waters. The major factors which explain the various loadings are precipitation and chemical weathering and anthropogenic. The results show that the groundwater in the study area is affected by the agricultural activities and in the downstream both anthropogenic and chemical weathering factors are found to be significant. The present state of the quality of the Rapine industrial area is of great concern and the higher concentration of toxic metals (Cr⁶⁺ and Fe²⁺) may entail various health hazards. Considerable decrease in concentration of cations and anions in the post-monsoon water samples indicates that the dilution factor predominates over the leaching factor. In the downstream of study area, the wells located in MGR Nagar contaminated by the leachate migration from chromium dump site in TCCL. If the leachate migration from chromium dump not intercepted at this stage it would further contaminate the groundwater reservoir posing a major threat to the entire living community of the area.

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