Hydrogeochemistry and Trace elements of Groundwater around Kelampakkam, Kancheepuram District, Tamilnadu, India

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Abstract:- **Water shortages have become an increasingly serious problem in India. Hydrogeochemical and trace elements of twenty two groundwater samples around Kelampakkam, Kancheepuram district is being analysed to know the quality of groundwater. Chemical properties have been established using major ions (cations and anions) and trace elements (Fe, Mn, Cr, Cu, Ni, Co, Pb and Cd). The results of the analyses were interpreted by various geochemical diagrams, like, Piper trilinear plot, Gibb's plot, Wilcox diagram, and USSL diagram. Alkaline exceeds alkalies and Strong acids exceed weak acids as 100% and 90.5% during pre and post-monsoon seasons. According to the Gibb's plot, most of the groundwater samples fall in the field of "rock water interaction" and few of the samples fall in anthropogenic activities during both seasons. The Wilcox diagram reveals that most of the samples fall in "very good to good" during pre-monsoon and post-monsoon of the study area. The USSL diagram reveals that most of the samples fall in C3S1 category during both seasons, which can be used for irrigation in almost all types of soil with little danger of exchangeable sodium.The order of trace elements during pre-monsoon is Fe>Pb>Ni>Co>Cd>Cr>Mn>Cu and during post-monsoon is Fe>Pb>Ni>Cr>Co>Cd>Mn>Cu. Excepting iron, all other trace elements are within permissible limit. Regarding iron, it ranges from 0.206 to 6.176 mg/l with an average value of 0.69 mg/l during post-monsoon and during pre monsoon it ranges from 0.01 to 4.976 mg/l with an average value of 0.60 mg/l in the study area. 9% of the samples (no. 13, 15 and 16) show Iron above permissible limit during both seasons and they are in the northwestern and southeastern part of the study area. The weathering of rock and discharge of waste effluents on the land are generally considered as the main source of iron in groundwater. The groundwater quality was found suitable for both irrigation and drinking purposes. The results demonstrate the need to monitor quality stratification and the changes in the groundwater baseline chemistry in the area.**

Keywords: Geochemistry; Groundwater; Trace elements; Piper trillinear; Gibb's plot; Wilcox diagram and USSL diagram.

I INTRODUCTION

Quality of groundwater is equally important to its quantity owing to the suitability of water for various purposes. Water quality analysis is an important issue in groundwater studies. Groundwater has come to play a major role in the life of the people, for it is used not only for drinking, but in industries and municipal purpose. India accounts for 2.2% of the global land and 4% of the world water resources and has 16% of the world's population. Groundwater occurs almost everywhere beneath the earth's surface not in a single widespread aquifer, but in thousands of local aquifer systems and compartments that have similar characters. The occurrence, replenishment, and recovery of groundwater have special significance in arid and semi-arid regions due to discrepancy in monsoonal rainfall, insufficient surface waters and over-drafting of groundwater resources. The quality of water is of vital concern for mankind, since it is directly linked to human welfare. It is generally recognized that the quality of groundwater in an area is as important as the quantity. Groundwater contamination is one of the most important environmental issues in the present world [1] in which metal contamination deserves major concern due to its high toxicity even at low concentration [2-3]. Variation of major elements in the groundwater can be controlled by cation exchanges, dissolution and precipitation of minerals, evaporation and oxidation-reduction reactions. It is subjected to a multitude of anthropogenic impacts attributable to accelerated population growth (7 million) and development of small-scale and large-scale industries, expansion of harbours and tourism related activities in the coastal zone, disposal of municipal wastes, industrial wastes and numerous recreational and commercial activities that not only degrade the quality of coastal water but also pose a serious health hazard to marine biotas and human [4-7]. Water pollution not only affects water quality, but also a threat to human health, economic development, and social prosperity [8]. Highly vulnerable to pollution due to absorption and transportation of domestic, industrial and agricultural waste water; therefore, it is significant to control water pollution and monitor water quality. Groundwater contamination is responsible for the change in the physical and chemical parameters. Variation in chemical composition of water is a function of its physical, chemical, biological and geological parameters which depend upon the soluble products of weathering and decomposition and the related changes that occur with respect to time and space. Municipal solid wastes can also contribute a considerable amount of metals to the groundwater through batteries, disposable household materials, plastics, paints and inks, body care products, medicines and household pesticides [9]. Though metals such as zinc, chromium, manganese, cadmium and cobalt play a biochemical role in the aquatic life, their excess presence is toxic and also non-biodegradable [10]. Many of the researchers have studied the contamination due to metal in both surface and groundwater [11-14] [8]. A few studies were conducted in Chennai for assessing the metal contamination [15-18]. Groundwater is the main source of water supply in this coastal region. The people of this area are facing acute fresh groundwater problems because most of the fresh water in these aquifers is being transformed into brackish and saline water. When seawater intrusion is a main cause of high salinity, groundwater generally exhibits high concentrations not only in total dissolved solids (TDS) but also in major cations and anions as well as accumulation of selected trace elements [19]. The current study is to assess the effects of natural and anthropogenic activities and increased human population on quality of groundwater and their variation by defining the principal hydrochemical analysis and trace elements of groundwater around Kelampakkam.

II STUDY AREA AND GEOLOGY

The study area is situated from Vandalur to Kelampakkam of Kancheepuram District, Tamil Nadu, India, a fast growing industrial area. It was a forest about 40 years ago. It was an intensely irrigated area. Agriculture was the major source of livelihood. The study area is shown in Fig (1). The district receives the rain under the influence of both Southeast monsoon (June-August) and Northeast monsoon (September-November). The weathered/fractured charnockite and alluvium form the major aquifer system. The Kancheepuram district is principally made up of hard rock and sedimentary formations overlaid by alluvium. Soils have been classified into: clayey soil, red sandy or red loamy, red sandy brown clayey soil, alluvial soil. The rock mass consists of quartz, feldspar, biotite and pyroxene. The alluvium and weathered crystalline charnockite form an aquifer system where ground water occurs in an unconfined condition. The major sources of groundwater recharge are precipitation. Alluvial deposits constitute the youngest formation consisting of sand and clays, occurring along the river courses. The shale and clay of Gondwana age occur on the bank of Palar river. Geology of the study area consists of Archean basement at the bottom, which is made up of Charnockites.

III MATERIALS AND METHODS

The water samples were collected from dug and bore wells in the study area using clear acid-washed polyethylene bottles. One liter of water samples were collected from each location from various wells during the month of June 2013 and January 2014 representing both Pre-monsoon and Post-monsoon seasons. Twenty two groundwater samples were collected for each of the seasons mentioned, for analysis of various physical-chemical parameters. pH was measured using portable pH meter and EC were measured by Electrode in the field itself. With respect to cations, Calcium, Magnesium were analyzed following volumetric method; Sodium, Potassium were analyzed by Flame photometer; and with respect to anions Chloride, Bicarbonate were done by volumetric method; Nitrate, Sulfate were estimated by turbidity method. Analyses were done following APHA method [20]. The analytical precision of the measurements of cations and anions were determined by calculating the ionic balance error that varies by about 5 to 10% [21]. The analytical data can be used for the categorization of water for utilitarian purposes and for ascertaining various factors on which the chemical characteristics of water depend.

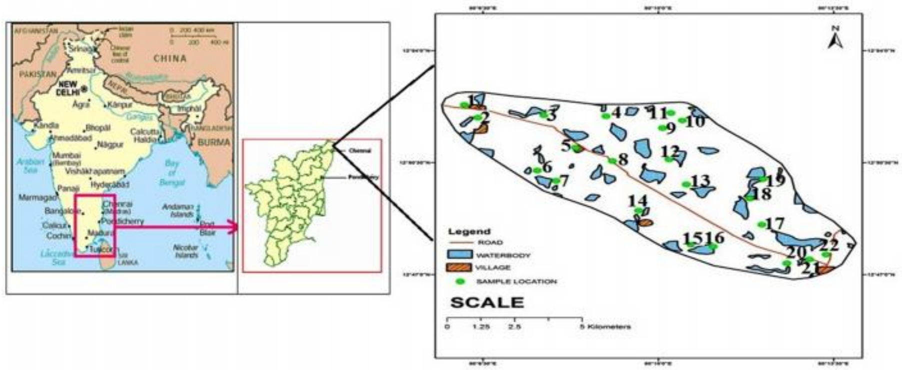


Figure.1. Study area map

IV RESULT AND DISCUSSION

Maximum and minimum concentration of major cations and anions of groundwater of the study area are presented in Table (1). Groundwater in the study area is generally alkaline in nature with pH ranging from 6.7 to 7.5 and 6.8 to 7.7 during pre and post-monsoon, respectively. EC is an indirect measure of ionic strength and mineralization of natural water. In the study area, EC ranges from 164 to 2530 µS/cm during pre-monsoon, while it ranges between 148 and 2300 µS/cm during post-monsoon. In the pre-monsoon season, the mean values of TDS varies from 115 to 1771 mg/l whereas, during the post-monsoon it ranges between 104 and 1610 mg/l. However, in some locations which are having clayey formations, TDS increases after rains that dissolve minerals from overlying material by infiltration.

Table 1 Maximum and minimum concentration of major cations and anions of groundwater samples during Pre and Post monsoon seasons

IONS	Pre monsoon		Post monsoon	
	Min	***Max***	***Min***	***Max***
pH	6.7	7.5	6.8	7.7
EC	164.0	2530.0	148.0	2300.0
TDS	115.0	1771.0	104.0	1610.0
Ca mg/L	17.0	232.0	19.0	240.0
Mg mg/L	6.0	70.0	3.0	70.0
Na mg/L	4.0	276.0	5.0	128.0
K mg/L	1.0	17.0	1.0	9.0
Cl mg/L	9.0	686.0	13.0	475.0
HCO_3 mg/L	44.0	528.0	40.0	780.0
SO_4 mg/L	2.0	61.0	3.0	77.0
TRACE ELEMENTS				
Fe mg/L	0.010	4.98	0.21	6.18
Mn mg/L	0.001	0.47	0.00	0.34
Cr mg/L	0.065	0.89	0.22	0.97
Cu mg/L	0.177	0.24	0.22	0.25
Ni mg/L	0.145	3.39	0.05	2.70
Co mg/L	0.002	2.06	0.01	0.75
Pb mg/L	1.128	3.84	1.22	3.69
Cd mg/L	0.029	0.97	0.07	0.59

A. Wilcox diagram

Sodium concentration is important in classifying the water for irrigation purposes because sodium concentration can reduce the soil permeability and soil structure [21-22]. The role of sodium in the classification of groundwater for irrigation was emphasized because of the fact that sodium reacts with the soil and as a result clogging of particles takes place, thereby reducing the permeability. Sodium with carbonate as the predominant anion, termed as alkali soils and chloride or sulfates as the predominant anion are termed as saline soil. Sodium-percentage determines the ratio of sodium in total cations including sodium, potassium, calcium and magnesium. All concentration values are expressed in equivalents per million. It is calculated as follows;

$$\text{Na \%} = \frac{(\text{Na+K}) * 100}{(\text{Ca+Mg+Na+K})}$$

Wilcox's diagram (Wilcox 1948), is adopted for the classification of ground waters for irrigation, wherein the EC is plotted against %Na. For the study area, the chemical data of pre and post- monsoon groundwater samples are plotted in the Wilcox's diagram Fig (2). It is observed that about 32% of the samples are "very good to good" and "good to permissible" category during pre-monsoon and 50% of the samples are "good to permissible" type during post-monsoon and one sample is "doubtful to unsuitable" category during post-monsoon of the study area.

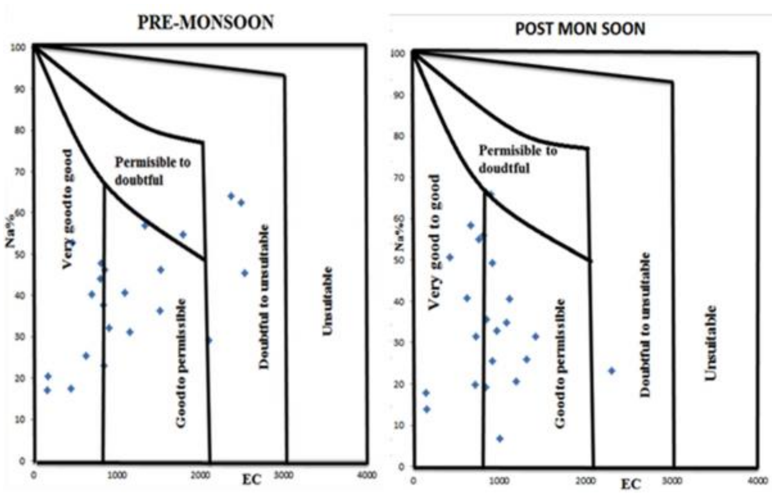


Figure 2. Wilcox diagram during pre and post monsoon seasons

B. USSL diagram

This diagram is used in interpreting the analysis of irrigation water. Water can be grouped into 16 classes. It uses Sodium Absorption Ratio in vertical axis and conductance in horizontal axis as shown in Fig (3). All concentration values are expressed in equivalents per million. Salinity, sodicity and toxicity generally need to be considered for evaluation of the suitability of groundwater for irrigation. Sodium absorption ratio is also used to determine the suitability of groundwater for irrigation as it gives a measure of alkali/sodium hazard to crops. If Calcium and Magnesium are dominant, the hazard is low. In the USSL diagram, S1, S2, S3, S4 types indicate sodium hazards and C1, C2, C3, C4 types indicate the salinity hazards. Based on this classification, majority of the samples belong to C2S1 (medium salinity, low sodium) and C3S1 (high salinity, low sodium) during pre and post monsoon seasons, respectively.

C. Gibbs diagram

The chemical relationships of groundwater based on aquifer lithology have been studied following Gibbs diagram (1970). Three kinds of fields are recognized in the Gibb's diagram, namely, precipitation dominant, evaporation-crystallization dominant, and rock-water interaction dominant. Gibbs plots for pre-monsoon and post monsoon are shown in Fig (4). According to the Gibbs diagram, for the study area, the rock–water interaction dominates the water chemistry in both seasons of the groundwater that fall under its influence for both the Gibb's ratios I-Na+K/ (Na+K+Ca) representing the cations and II- Cl/ (Cl+HCO_3) representing the anions. The rock–water interaction dominance field indicates the interaction between rock chemistry and the chemistry of the percolation waters under the subsurface.

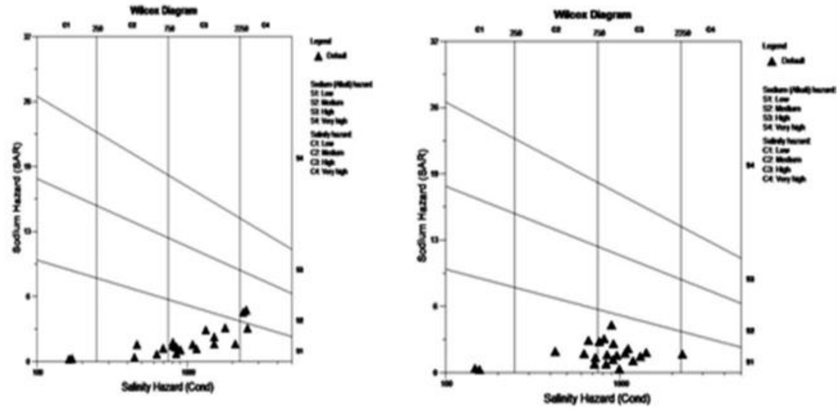


Figure 3. USSL diagram during pre and post monsoon seasons

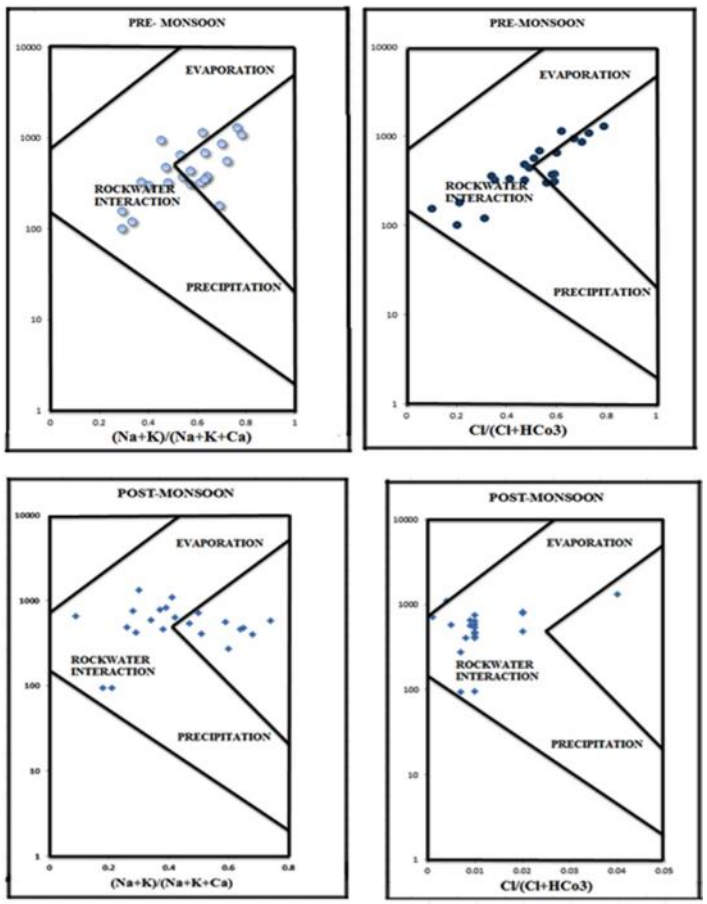


Figure 4. USSL diagram during pre and post monsoon seasons

D. *Hydrochemical facies*

The concentrations of major ionic constituents of groundwater samples were plotted in the Piper diagram to determine the water types. The classification for the cation and anion facies, in terms of major ion percentages and water types, is according to the domain in which they occur in the diagram segments. To define a composition class, Back and Co-workers suggested subdivisions of the tri-linear diagram. The cations and anion fields are combined to show a single point in a diamond-shaped field, from which inference is drawn on the basis of hydrogeochemical facies concept. It clearly explains the variations or domination of cation and anion concentrations during pre and post-monsoon as shown in Fig (5). Alakline earth (Ca+Mg) exceeds alkalies (100%) and (90.5%) and the type Strong Acids exceeds weak acids (63%) respectively based on hydro-chemical facies as shown in Table (2) . Rapid urbanization and industrialization make an impact on groundwater quality of the study area. The reason is groundwater passing through igneous rocks dissolves only small quantities of mineral matters because of the relative insolubility of the rock composition.

Table 2 Characterization of groundwater of the study area using Piper diagram

Subdivision of the diamond	Characteristics of corresponding subdivisions of diamond shaped fields	Percentage of samples in this category (Pre-Monsoon)	Percentage of samples in this category (Post-Monsoon)
1	Alkaline earth (Ca+Mg) Exceed alkalies (Na+K)	100	90.5
2	Alaklies exceeds alkaline earths	00.0	9.00
3	Weak acids (CO_3+HCO_3) Exceed Strong acids (SO_4+Cl)	27.2	36.3
4	Strong acids exceeds weak acids	72.7	63.6
5	Magnesium bicarbonate type	27.2	36.6
6	Calcium-chloride type	13.6	27.2
7	Sodium-chloride type	00.0	00.0
8	Sodium-Bicarbonate type	00.0	00.0
9	Mixed type (No cation-anion exceed50%)	59	45.4

E. Iron and Manganese

The iron concentration in the groundwater of the study area during pre monsoon ranges from 0.01 to 4.976 mg/l with an average value of 0.60 mg/l. During post monsoon it ranges from 0.206 to 6.176 mg/l with an average value of 0.69 mg/l. During both seasons, the highest value is recorded at Talynucheri (sample no. 16). The spatial distribution of Fe concentration in ground water is presented in Fig (6) for pre and post monsoon. It shows the high concentration in Southern part of the study area during pre and the post monsoon seasons. In general, rock water interaction and agricultural activities are the major source for high concentration of iron in the study area. The weathering of rock and discharge of waste effluents on the land are generally considered as the main source of iron in groundwater. Dissolved carbon dioxide, pH and EC of water affect the nature of aqueous iron species present in the water.

The concentration of Manganese in the groundwater of the study area during pre monsoon ranges from 0.001 to 0.472 mg/l with an average value of 0.110 mg/l. The highest values were recorded in the pre monsoon period of the study area at Madurapakkam (sample no. 11). During post monsoon it ranges from 0.001 to 0.336 mg/l with an average value of 0.05 mg/l.

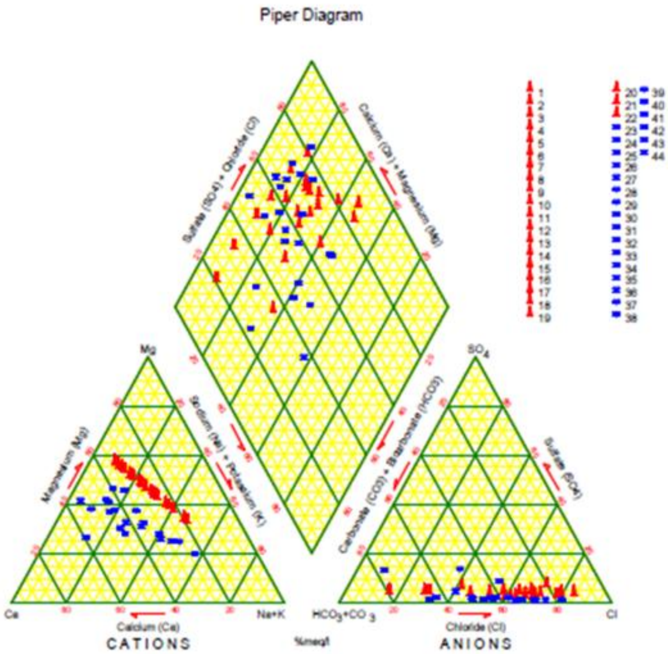
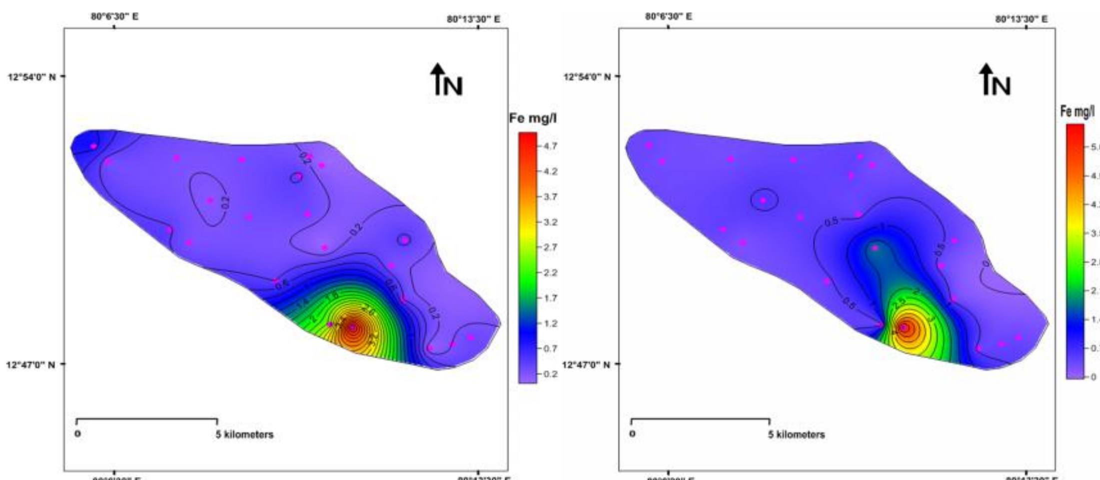


Figure 5. Ppier during pre and post monsoon seasons



pre monsoon post monsoon

Figure 6. Spatial distribution of Fe concentration during pre and post monsoon seasons

F. Lead and Cadmium

The concentration of Lead in the groundwater of the study area during pre monsoon ranges from 1.128 to 3.835 mg/l with an average value of 2.25 mg/l. The highest value is recorded in the pre monsoon period of the study area at Kulathur (sample no. 14). During post monsoon it ranges from 1.218 to 3.686 mg/l with an average value of 2.856 mg/l. The highest value is recorded in the post monsoon period of the study area at Velichchai (sample no. 8).

The concentration of Cadmium in the groundwater of the study area during pre monsoon ranges from 0.029 to 0.965 mg/l with an average value of 0.482 mg/l. The highest value is recorded in the pre monsoon period of the study area at Ichchikadu (sample no. 18). During post monsoon it ranges from 0.074 to 0.587 mg/l with an average value of 0.228 mg/l. The highest value is recorded in the post monsoon period of the study area at Sirucheri (sample no. 19). Cadmium can also enter the environment from a variety of industrial applications, including mining and smelting, electroplating, and pigment and plasticizer production. Drinking water is generally contaminated with galvanized iron pipe and plated plumbing fittings of the water distribution system.

G. Chromium and Copper

The concentration of Chromium in the groundwater of the study area during pre monsoon ranges from 0.065 to 0.892 mg/l with an average value of 0.419 mg/l. The highest value is recorded in the pre monsoon period of the study area at Kulathur (sample no. 14). During post monsoon it ranges from 0.216 to 0.972 mg/l with an average value of 0.576 mg/l. The highest value is recorded in the post monsoon period of the study area at Sonallur (sample no. 13). The concentration of Copper in the groundwater of the study area during pre monsoon ranges from 0.177 to 0.236 mg/l with an average value of 0.204 mg/l. The highest value is recorded in the pre monsoon period of the study area at Kelambakkam (sample no. 22). During post monsoon it ranges from 0.215 to 0.249 mg/l with an average value of 0.231 mg/l.

V CONCLUSION

The hydrogeochemistry of the study reveals that the groundwater in the Kelampakkam is alkaline in nature. According to the Willcox's diagram, 32% of the samples are "very good to good" and "good to permissible" category during pre-monsoon and 50% of the samples are "good to permissible" type during post-monsoon and one sample is "doubtful to unsuitable" category during post-monsoon. From USSL diagram, the majority of the samples belong to C2S1 (medium salinity, low sodium) and C3S1 (high salinity, low sodium) during pre and post monsoon seasons, respectively. The abundance of major cations is in the order of Ca>Na>Mg in both seasons. The abundance of major anions is in the order of Cl > HCO_3 >SO_4 during both seasons. According to the Gibbs diagram, the rock–water interaction dominates the water chemistry in both seasons of the groundwater that fall under its influence for both the Gibbs ratios I-Na+K/ (Na+K+Ca) representing the cations and II- Cl/ (Cl+HCO_3) representing the anions. Alakline earth (Ca+Mg) exceeds alkalies (100%) and (90.5%) and the type Strong Acids exceeds weak acids (63%) respectively based on hydro-chemical facies.

Rapid urbanization and industrialization make an impact on groundwater quality of the study area. The order of trace elements during pre-monsoon is Fe>Pb>Ni>Co>Cd>Cr>Mn>Cu and during post-monsoon is Fe>Pb>Ni>Cr>Co>Cd>Mn>Cu. Excepting Iron, all other trace elements are within permissible limit. 9% of the samples are above the permissible limit during both seasons. Iron values were above permissible limit in northwestern and southeastern part of the study area during both seasons. The weathering of rock and discharge of waste effluents on the land are generally considered as the main source of iron in groundwater. The reason is groundwater passing through igneous rocks dissolves only small quantities of mineral matters because of the relative insolubility of the rock composition. Anthropogenic activities have taken place in the study area which causes harmful effect on the groundwater due to the industrial, domestic sewage water discharge and seawater intrusion.

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