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A Comprehensive Geochemical Evaluation of the Water Quality of River Adyar, India

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Abstract The River Adyar flows through the fault of south Chennai for about 50 Km and enters into the Bay of Bengal. This river is almost stagnant and do not carry enough water except during rainy season. Rapid industrialization and urbanization along the river course during 80s and 90s of last century has increased the pollution of the river water. The main objective of this study is to identify and assess the nature of pollution. In order to achieve this objective, necessary geochemical parameters were determined and the quality of water is evaluated using various tools, such as Wilcox diagram, USIS, Piper, sodium absorption ratio (SAR), 3D scattered diagrams, and seasonal variation diagrams. The monsoonal variations in the data matrix of the river water (River Adyar) was monitored at 33 stations for the premonsoon and postmonsoon periods during September 2005 and February 2006.

Keywords Water quality · River Adyar · Trace metal chemistry · Geochemistry

River water studies have received wide attention due to the need to understand the weathering, hydrological, seasonal, and anthropogenic factors which influences the water quality. Urban rivers have been associated with water quality problems and the practice of discharging untreated domestic and industrial waste into the water course has recently been emerged. High population density in Chennai increases the pressure on the drainage system and sewage treatment plants. The existing system does not cope up with the heavy domestic discharge and at many points, domestic effluents are directly directed into the river water which leads to the present level of degradation of River Adyar. If the quality of water deteriorates, it will naturally affect the soil–plant–water system and human health conditions. Hence periodical monitoring of the water quality gains significance.

Rivers play a major role in assimilating or carrying of industrial and municipal wastewater, run-off from agricultural fields, roadways and streets, which are responsible for river pollution. The discharge of industrial and municipal waste-water can be considered as a constant polluting source, but not so the surface runoff which is seasonal. The seasonal variation study of the river water throws more light on the hydrogeochemistry of the river and also helps to evaluate the interdependencies and inter-relationships of various ions present in this water. In order to achieve this objective, the river water samples were collected at 33 stations during two monsoon periods and the physico-chemical parameters were evaluated. Gibbs diagrams are used to determine the source of chemical budget of the ions in the river water. Moreover, the suitability of the river water to irrigation was studied using various tools viz., Wilcox diagram, salinity diagram, and sodium absorption ratio (SAR).

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Materials and Methods

The river water (Fig. 1) samples were collected from surface at a depth of 0.3 m during premonsoon (September 2005) and postmonsoon (February 2006) in new 1-L HDPE bottles rinsed three to four times with the water sample before filling it to capacity and then labeled accordingly. In each station, samples were collected in duplicate and prior to analysis in the laboratory, they were stored at a temperature below 4°C.

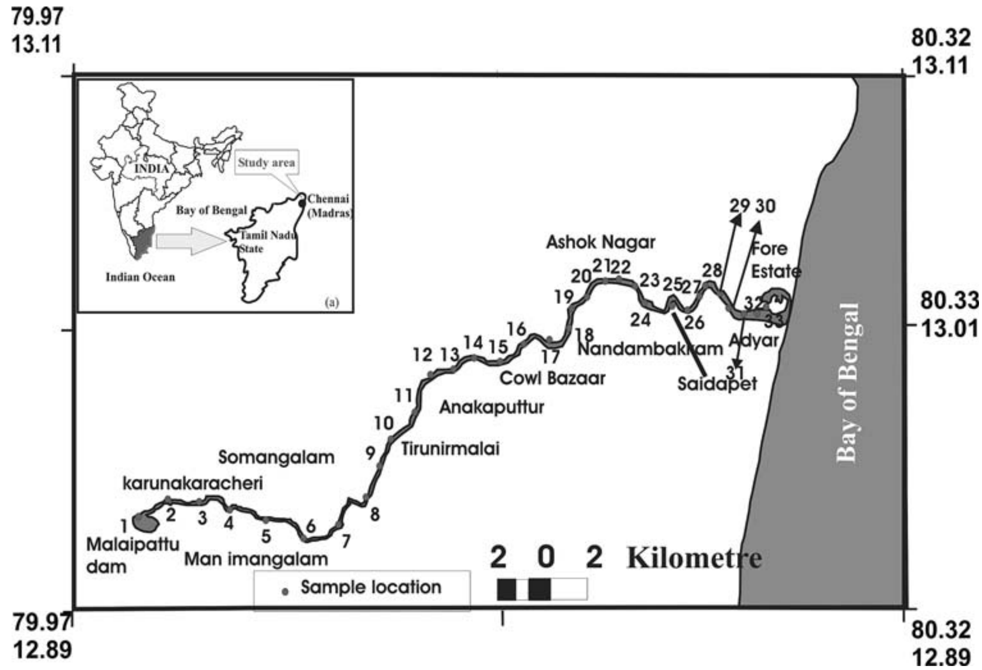


Fig. 1 Base map of River Adyar

EC and pH of water samples were measured in the field immediately after the collection of the samples using pH and Electric Conductivity meters. Na^+ and K^+ were measured by using a flame photometer (Model: Systronics Flame Photometer 128). Silica content was determined by Molybdate Blue method using UV–Visible spectrophotometer. Total dissolved solids (TDS) were measured by evaporation and calculation methods (Hem 1991). Ca^{2+} and Mg^{2+} were determined titrimetrically using standard Ethylene diamine tetra acetic acid (EDTA). Chloride was estimated by $AgNO_3$ titration. Sulphate was analyzed using the turbidimetric method (Clesceri et al. 1998). Nitrate, nitrite, phosphate, fluoride were analyzed using UV–Visible spectrophotometer. Standard solutions for the above analysis were prepared from the respective salts of Analytical Reagent grade. Trace metals were determined by Graphite Furnace Atomic Absorption Spectrophotometer (Perkin-Elmer AAnalyst 700). Quality of the results was ensured by testing the duplicates of the samples for every 10 measurements. Moreover, the results of the field sample duplicates were compared and found to be of almost similar value. The average value of these two results was taken for further interpretation. Multi element Perkin-Elmer standard solutions were used for the estimation of trace metals.

Results and Discussion

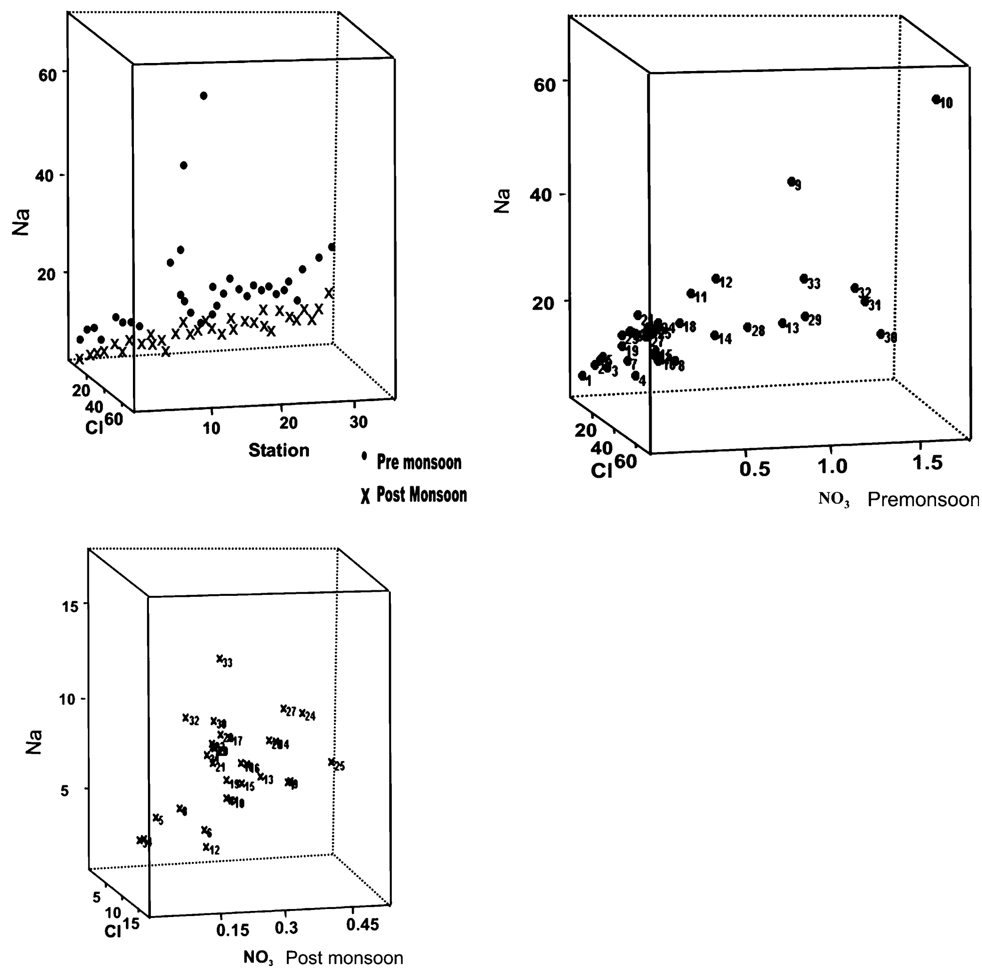
The analytical data of the river water is summarized in Table 1. The results reveal that many of the stations demonstrate slightly acidic behavior except at few stations in the upper course of the river where the water was found to be alkaline. However, during the postmonsoon, pH of water in all the stations was found to be alkaline. In the case of TDS, there is a considerable amount of dilution of concentration of ions during the postmonsoon due to precipitation. Higher concentration of TDS is observed in the river water near the middle part of the river basin at stations 9 and 10. Various industries, such as dyeing, tanning, and pharmaceutical industries are concentrated in these areas. The effluents from these industries are directed into the river course which increases the concentration of ions in the water. During premonsoon, the ionic concentrations of Ca^{2+}, Mg^{2+}, Na^+, and K^+ (based on mmol/L) are 16.22%, 6.41%, 73.37%, and 4.00% and the order of abundance is $Na^+ > Ca^{2+} > Mg^{2+} > K^+$. But during postmonsoon, the ionic concentrations (based on mmol/L) are 22.35%, 18.72%, 56.8%, and 2.13% and the order of abundance remains the same. Similarly in the case of anions during premonsoon, the ionic concentrations of HCO_3^-, SO_4^{2-}, Cl^- (based on mmol/L) are 20.02%, 9.94%, and 70.05% and the order of abundance of anions is $Cl^- > HCO_3^- > SO_4^{2-}$. During postmonsoon, the ionic concentrations of HCO_3^-, SO_4^{2-}, Cl^- (based on mmol/L) are 31.98%, 8.67%, and 59.35% and there is no change in the order of abundance. The seasonal effect is found to be apparent in the chemical budget of water though it does not affect the order of abundance of ions during pre and postmonsoon periods.

The 3D scattered diagram (Fig. 2) demonstrates marked difference for both the seasons. The variation of Na and Cl with regard to the stations shows that there is a linear relationship with positive slope which indicates that the concentration of these ions increases from the upper part of

Table 1 Summary statistics of analytical data

Parameters in μg/mL	Minimum		Maximum		Mean	
	Premonsoon	Postmonsoon	Premonsoon	Postmonsoon	Premonsoon	Postmonsoon
pH	6.2	7.36	8.92	9.1	7.00	8.47
EC (μS)	1189	584.4	7944	3216	2978	1784
TDS	761	374	5084	2058	1906	1142
Ca	32	48	288	216	154.6	111
Mg	9.6	9.6	67.2	105.6	37.06	56.4
Na	126.4	27.27	1750	389	436.1	176
K	11.5	0	58.97	34	37.21	10.35
HCO_3	98	73.2	464	542	314.5	289.9
SO_4	207.3	41.77	318.6	174	245.8	123.8
Cl	120	120	2500	627	639.4	312.6

Fig. 2 3D scatter diagrams



the river to the confluence point. In premonsoon, (Fig. 2) illustrates the variation of Na and Cl with regard to Nitrate. If the variation of Na with Cl is related to NO_3, then the contribution of anthropogenic activities is highly expected. From the diagram, it is clearly seen that from the middle part of the river up to the confluence point, the alkali–halide ion is increasingly related with the nitrate ion reflecting that the river water in these regions are affected due to anthropogenic activities especially the mixing of sewage water into the river water. During postmonsoon, the variation of Na and Cl with nitrate is only moderate indicating the predominance of dilution of the point sources of pollution.

The nature and type of water can be evaluated by plotting the concentration of major cations and anions in the piper diagram (Fig. 3a). The plot shows that most of the river water samples analyzed during the premonsoon fall in the field of CaMgCl and few of the samples demonstrates NaCl and CaCl types. In the case of postmonsoon, it has been observed a clear shift from CaMgCl to NaCl type. Most of the samples show NaCl type and a few samples reveals CaMgCl type. From the plot, it is observed that alkalis (Na^+ and K^+) exceed the alkaline earths (Ca^{2+} and Mg^{2+}) and Cl^- exceeds the other anions.

Metals enter into river water from a variety of sources, such as chemical weathering of rocks and soils, dead and decomposing vegetation and animal matter, wet and dry fallout of atmospheric particulate matter and from man's activities including the discharge of various domestic and industrial effluents. Though trace metals such as zinc, chromium, manganese, cadmium, cobalt, etc. play a biochemical role in the aquatic life, their excess presence is toxic and also non-biodegradable (Nurnberg 1982).

The water quality of River Adyar is affected by factors, such as return flow of agricultural drainage water, industrial, and domestic waste discharges directly directed into the river water and decline of the river velocity to almost stagnation in urban areas. The quality of water with regard to the concentration of trace metals (Cu, Co, Zn, Fe, Pb, and Cr) is assessed and the seasonal variation of the metals was evaluated in the river water samples (Fig. 4). The Cu values ranges from 0.031 to 0.568 mg/L with an average value of 0.08 mg/L during premonsoon. However, the postmonsoon values range from 0.011 to 0.143 with a mean of 0.070. Both in pre and postmonsoon, the concentration of Cu is well within the World Health Organization (WHO) allowed limit. The range obtained was lower than the permissible value and hence adverse effects from domestic use are not expected as far as this metal is concerned. Station 8 shows high Cu where extensive farming is practiced and it is expected that Cu may enter into the aquifers through agrochemicals. The concentration of cobalt during premonsoon ranges from 0.001 to 0.094 mg/L with a mean of 0.040 and the postmonsoon shows 0.001–0.080 mg/L with a mean of 0.020 mg/L. The maximum permissible limit of Co is 0.05 mg/L. The results shows that 15 stations crosses the WHO allowed limit but none of the stations show extreme values. Zinc ranges from 0.001 to 1.315 with a mean of 0.080 mg/L during premonsoon and postmonsoon demonstrates 0.001–0.070 with a mean of 0.020 mg/L. The concentration of zinc in these waters during both the seasons has not crossed the prescribed limit of 3 mg/L. The relatively higher concentrations of zinc in some of the stations of the study area may be attributed to the presence of unused remains of zinc sulfate, which is an important constituent of fertilizers used in the region. The concentration of Fe in many of the stations is higher than the WHO permitted limit of 0.3 mg/L. The average value during pre and postmonsoon is 0.78 and 0.43 mg/L, respectively. The high Fe concentration in these waters may be assigned to the soil–water interaction especially in the middle part and in the lower part of the river stretch where it is observed that the water is almost stagnant facilitating the dissolution and concentration of the ions in the river water. Pb values during premonsoon ranges from 0.035 to 0.658 with a mean of 0.23 mg/L and the values of postmonsoon ranges from 0.002 to 0.564 with a mean of 0.180. Lead is usually found in low concentration in natural waters because Pb containing minerals are less soluble in water. Concentration of lead in natural water increases mainly through anthropogenic activities. Almost all stations show the concentration of Pb higher than the WHO allowed limit of 0.01 mg/L in premonsoon which may create health hazards. The concentration of various industries along the middle part of the river course and their activities should have increased the higher concentration of lead in the river. Moreover, the atmospheric depositions resulting from the automobile pollution and the urban runoff due to precipitation may also leads to the increase in the concentration of Pb in the aquifers. The value of Cr ranges from 0.024 to 1.289 with an average value of 0.61 during premonsoon and 0.029–1.025 with an average value of 0.46 during postmonsoon. Except station No. 24, all other stations show higher concentration of Cr in the water. The concentration of various industries, such as tanneries, chrome plating and dyeing industries near the river stretch especially in the middle part of the river contributes to the river chemistry.

The evaluation of water quality was carried out in order to identify its suitability to drinking and irrigation purposes. The major factors which decides the quality of the water in the study area is agricultural activities near the upper stretch of the river, rock–water interaction, anthropogenic activities at the middle and lower part of the river and saline water intrusion near the confluence point. Except at few stations, the pH (6.2–9.1) of the water samples during pre- and postmonsoons is within the safe limits (6.5–8.5) prescribed for drinking water by WHO (1984). Except at few stations, the concentration of TDS (374–5084 mg/L) is more than the recommended limit of 1,000 mg/L allowed (WHO 1984) in all water samples during both the seasons especially in the case of premonsoon which may cause gastrointestinal irritation to the consumers.

In order to assess the water suitability to irrigation, Percent sodium, SAR and Wilcox diagrams (Fig. 3c) are

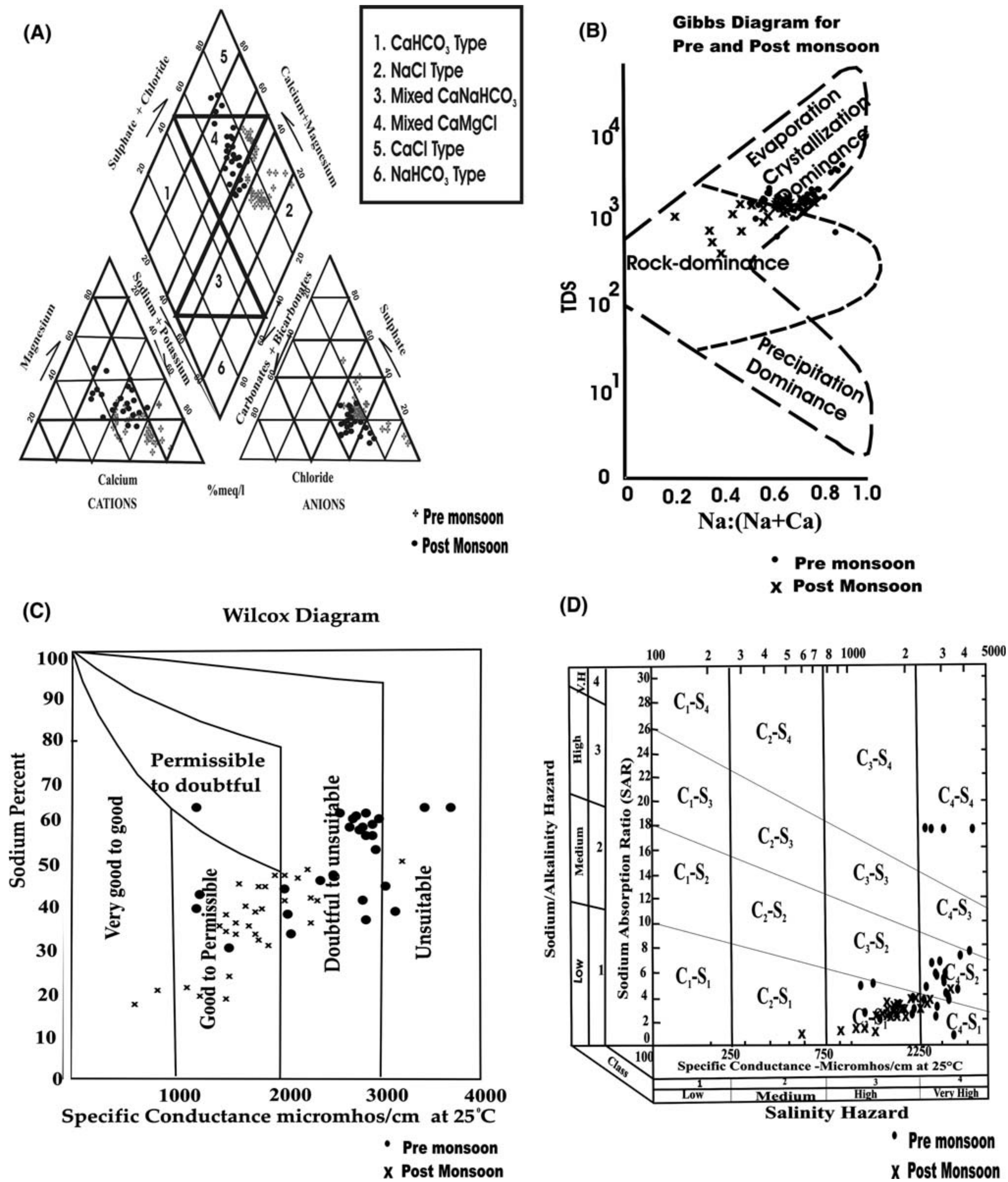
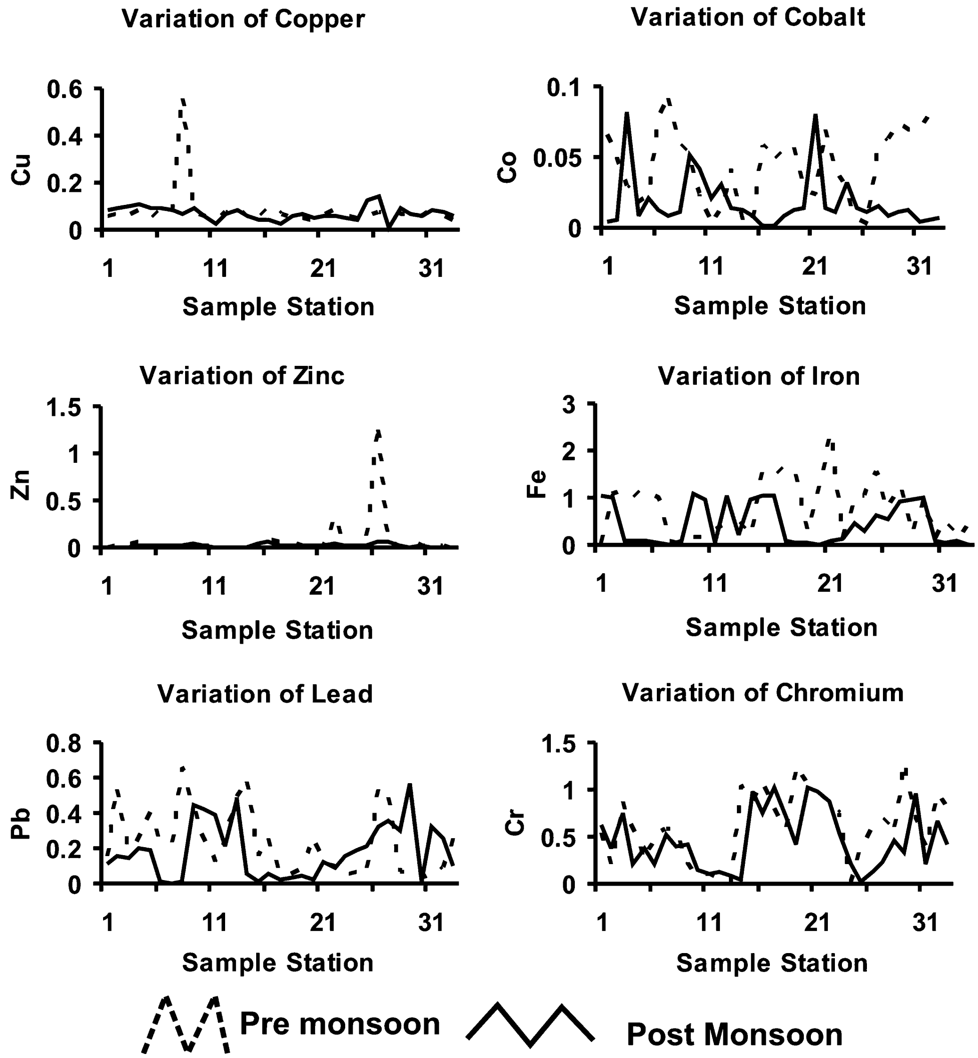


Fig. 3 (**a**) Piper diagram representing hydrochemical facies. (**b**) Specific conductance and % sodium relation for rating irrigation water (Wilcox 1955). (**c**) Rating of water samples in relation to salinity and sodium hazard (USSL 1954). (**d**) Mechanism controlling groundwater quality (Gibb's diagram)

evaluated. Wilcox (1955) used % sodium and specific conductance in evaluating the suitability of water to irrigation. Sodium-percentage determines the ratio of sodium to the total cations viz., sodium, potassium,

Fig. 4 Seasonal variation of trace metals



calcium, and magnesium. The result shows that the water near the upstream is good for irrigation and the contamination are found to be high near the downstream. During premonsoon, only 9% shows good to permissible for irrigation; 59% falls in the region of doubtful to unsuitable; 21% falls under the unsuitable region. This may be due to the increased anthropogenic activities near the middle and downstream owing to intense settlements along the bank of the river, directing the domestic sewage into the river and saline water intrusion. The results shows that 60% of the water values illustrate good to permissible; 21% falls in the region of doubtful to unsuitable; 12% of the water are unsuitable for irrigation. Postmonsoon demonstrates values favorable to irrigation indicating that there is an extensive dilution of the river water during this period.

Another important tool commonly used to assess the degree of suitability of water to irrigation is SAR. It has been found that the magnitude of absorption of Na^+ by soils has a direct relationship with SAR. Higher concentration of Na^+ in soils saturates the ion-exchange complex with Ca^{2+} resulting in deflocculation, impermeability and cultivation in such soils becomes very difficult (Subba Rao 2006). The SAR concentration ranges from 1.66 to 17.12 with a mean of 6.80 for premonsoon and from 0.48 to 4.26 with a mean of 2.19 in post monsoon. The results shows that 12 samples in pre monsoon and no samples in post monsoon shows SAR values >6. Water containing SAR values >6 have higher concentration of Na^+ relative to the concentration of Ca^{2+} reflecting that this water is not suitable for irrigation.

Electric conductivity (EC) is a good measure of salinity hazard to crops as it reflects the TDS in groundwater. Graphical representation (Fig. 3d) of the chemical data on the irrigation suitability diagram (Richards 1954) clearly brings out the seasonal variation and the suitability of the water to irrigation. During premonsoon, the US salinity diagram demonstrates that the river water samples fall in the fields of C_3S_1, C_4S_1, C_4S_2, and C_4S_4. About 45% of the samples falls in the field of C_3S_1 and C_4S_1 reflecting high salinity and low sodium water which can be used for irrigation on almost all types of soil with only a minimum risk of exchangeable sodium. The water of this type can be used for plants having good salt tolerance (Karanth 1989). Samples belonging to high salinity-medium sodium (C_4S_2) need adequate drainage to overcome the salinity problem. Samples falling in the C_4S_4 are not suitable for irrigation. In the case of postmonsoon, US salinity diagram illustrates that most of the samples fall in the fields of C_3S_1 and C_4S_1. About 85% of the samples show high salinity−low sodium (C_3S_1) and remaining samples falls in the C_4S_1 region clearly demonstrating the seasonal variation and the requirement adequate drainage for irrigation.

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