

EVALUATION OF SEASONAL EFFECTS ON THE QUALITY OF SHALLOW GROUNDWATER IN THE VICINITY OF ASA RIVER, ILORIN, SOUTHWESTERN, NIGERIA

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ABSTRACT

Hydrochemical investigations of the groundwater and the seasonal effects on the chemical budget of ions along the course of the Asa were carried out. This was aimed at studying the effects of the river water on the nearby groundwater, determining the major ions and their origin, and determining the suitability of the river water for domestic and irrigation purposes. Twenty-three water samples were collected during dry and wet seasons from wells adjacent to the river at depth of 10ft to 20ft. Electrical conductivity and PH were measured in situ while other hydrochemical analyses were carried out in the laboratory. The suitability of the river water for irrigation purposes was evaluated using Wilcox's, diagram, Kelly's and Magnesium ratio. The source of the ions in the water was examined and classified using the Gibb's diagram. The hydrochemical analysis results indicated sodium and chloride as the most predominant ions. The nitrate concentration ranged from 4.2mg/l to 45.9mg/l and 1.02mg/l to 75.9mg/l respectively in the dry and wet season. Piper's diagram showed predominance of NaCl and CaMgCl. The Gibb's diagram revealed that the TDS values of the dry season were lower than the wet season. The order of abundance of the cations during the dry and wet season were respectively $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$ the anions were of the order of $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^-$ in both dry and wet seasons. A comparison of the groundwater standard showed that the water samples are not suitable for drinking especially during wet season. The hydrochemical investigation has shown that the seasonal effect does not change the order of abundance of the major ions but change the order of abundance of major cations. The water also was neither suitable for drinking nor irrigation.

Keywords: Hydrochemical, Asa River, Chemical budget, Groundwater, Piper diagram, Irrigation.

INTRODUCTION

Rapid Urbanization and increased agricultural activities have resulted in the degradation of the water quality. Used and unused fertilizers, pesticides, effluents discharged from industries and sewage water are the main contaminants of the groundwater in the vicinity of rivers that flow through populated area (Chandu *et al.*, 2008). Asa river in Ilorin southwestern Nigeria flows north-south and divides the city into almost 2 equal halves (East-West). The river and its banks have been turned into waste dumpsite by the inhabitants at the floodplain. Petroleum waste from the vehicle mechanic workshops which are situated close to the river are poured directly in to the river. The wastes eventually percolate into the shallow groundwater system and pollute the water body.

During the dry season, the tributaries become almost dry and the predominantly sandy bottom of the stream bed is littered with scattered ponds, containing mainly waste water. As a result of lack of flowing discharge during this period, household-and industry-borne chemicals and other pollutants such as grease, sewage water and bacteria pollute the vicinity of the river (Alao and Ige, 2003). Thereon, most of the hand-dug wells in Ilorin metropolis with depth ranging from 5m to 8m deep have been polluted by the migration of pollutant into the shallow aquifers (Olasehinde *et al.*, 1998). The present study therefore involves hydrochemical investigation of groundwater and seasonal effect on the chemical budget of ions along the course of Asa River. The main objectives are to study the effect of the river water on the nearby groundwater, determine the major ions and their origin, determine the stability of the river water for irrigation and drinking purposes.

Description and Geology of the Study Area

The study area is Ilorin metropolis which is the capital city of Kwara state, Nigeria and bounded by latitude $8^\circ 20'N$ and $8^\circ 40'N$ and longitude $4^\circ 30'E$ and $4^\circ 40'E$. In this study, the groundwater samples in the proximity (Figure 1) of Asa River were taken for chemical analysis. Asa River, flowing north-south direction divides the city of Ilorin almost to two equal halves. The river and its banks have been turned into waste dumpsite by the inhabitant of the floodplain. Petroleum waste from the motor mechanic workshops which are located close to the river are poured directly into the river and eventually percolate into the shallow groundwater system thereby polluting the groundwater body.

Geologically, the study area is underlain by the Precambrian basement complex rocks that include: the granites, granitic gneiss and Migmatite (Annor *et al.*, 1996). The rock form part regional north-western Island running northwest-southeast parallel to the river Niger (Offodile, 1987; Annor *et al.*, 1996). Ilorin is situated on

the northern boarder of this prominent large scale morphological feature on an elevation of about 330m asl. The area is mainly drained northwards by the Asa and Oyun rivers and their tributaries. For a short period in the year, December to March, the Asa River may have little or no discharge because the available water is kept in the dam reservoir, 2km south of the city. Also the tributaries become almost dry after the wet season, during which the predominantly sandy bottom of the stream bed can be seen and water is found only in scattered ponds. Therefore, waste water from household and industries may be the only contributors to the streams at such periods. Hence, due to lack of flowing discharge, household and industry- borne chemicals and other pollutants like grease, sewage water and bacteria, pollute the vicinity of the river (Alao and Ige, 2003).

MATERIALS AND METHODS

Twenty-three groundwater samples were collected during January 2001 and September 2001 representing dry and wet seasons to evaluate the seasonal variations in chemical compositions. The water samples were collected from wells adjacent to the river at a depth of 10 to 20 ft. The samples were collected in new HDPE bottles dry-washed with dilute hydrochloric acid and rinsed three to four times with the water sample before filling it to capacity and labeled accordingly. The samples were stored at a temperature below 4°C prior to analysis in the laboratory. For collection, preservation and analysis of the samples, the standard methods (AWWA, 1971; APHA, 1995) were followed. Electrical Resistivity (EC) and pH of water samples were measured in the field immediately after the collection of the samples using portable field electrical conductivity and pH meters. Na^+ and K^+ were measured by using a flame photometer (Model: Systronics Flame Photometer 128). Total dissolved solids (TDS) were measured by evaporation and calculation methods (Hem, 1991). Ca^{2+} and Mg^{2+} were determined titrimetrically using standard EDTA. Chloride was estimated by AgNO_3 titration. Sulphate was analysed using the turbidimetric method (Clesceri *et al.*, 1998). Nitrate, nitrite, phosphate, fluoride were analysed using UV-visible spectrophotometer (Rowell, 1994).

RESULTS AND DISCUSSION

(a) Chemistry of groundwater

The summary of the statistical analyses of the groundwater parameters are as shown in table 1 and 2 for dry and wet season respectively. The seasonal variation of the various chemical parameters in the groundwater of the study area is as shown in Figure 2.

The pH values of groundwater are slightly acidic, ranging from 6.0 to 6.7 with an average value of 6.3 during dry season. However during the wet season, the pH of groundwater was found to be alkaline ranging from 7.2 to 9.0. In both seasons the concentration of TDS ranges from 1680 to 5120 mg/l with a mean of 1733.1mg/l in dry season and 420 to 8806 mg/l with a mean of 2277.2 mg/l in wet season. There was a considerable increase in the concentration of ions during the wet season and the increase in the ionic concentration may be essentially due to the anthropogenic activities. During wet season the water table in the study area is nearer to the surface and active leaching and subsequent infiltration would have changed the chemical composition of groundwater.

According to Fetter (1990), most of the groundwater samples collected in the area during the dry season and wet season periods belong to brackish type ($\text{TDS} > 1,000\text{mg/l}$). During dry season, the concentration of cations Ca^{2+} , Mg^{2+} , Na^+ , K^+ ions hovers between 56.0 to 208.0; 16.4 to 120.6; 136.3 to 795.0; 0 to 44.2mg/l with a mean of 125.0, 55.6, 312.0 and 13.0 mg/l respectively. The order of abundance is $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$. However, during wet season the concentration of cations Ca^{2+} , Mg^{2+} , Na^+ , K^+ ions ranged from 48.0 to 424.0; 12.0 to 686.0; 31.8 to 120; 0 to 64.8mg/l with a mean of 197.7, 134.2, 391.3 and 11.3mg/l respectively. The order of abundance is $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$. The seasonal change has the effect on the order of abundance of major ions. Similarly in the case of anions during dry season, HCO_3^- , SO_4^{2-} , Cl^- , NO_3^- are in the order of 224.8 to 1037.0, 204.0 to 292.0, 110.0 to 121.0 and 4.2 to 45.9mg/l with a mean of 375.4, 238.6, 435.4 and 18.4mg/l respectively. The order of abundance is $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^-$. During the wet season HCO_3^- , SO_4^{2-} , Cl^- , NO_3^- ranged from 170.8 to 732.0, 32.4 to 272.0, 150.0 to 3470.0, 1.0 to 76.0 mg/l with a mean of 368.9, 176.7, 956.9 and 21.1 mg/l respectively. The order of abundance is $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^-$.

Fluorides varied from 0.5 to 2.0mg/l with a mean of 1.12mg/l in dry season and during wet season it varied from 0.2 to 1.0 with a mean of 0.5mg/l. This indicates the dilution of the concentration of fluorides during wet season. A t-test was performed to determine the effect of season on the chemical constituents (variables) present in the groundwater. The results show that Na^+ , K^+ , Cl^- , HCO_3^- , F^- , NO_2^- and NO_3^- and PO_4^{3-} are found to be non-significant with respect to seasonal changes. A t-value for pH is found to be very high since the season changes the pH value of this groundwater from acidic to alkaline. Standard deviation results show that the TDS values exhibit high variability in both dry and wet season periods.

The cause of this variability may be due to the difference in the chemical constituents of the groundwater near the fresh water river (lower) course and the groundwater near the saline estuarine water (middle-upper course). The above fact is substantiated by the high standard deviation values of the sodium and chloride concentration. During wet season, nitrate values at three stations (stations, 17, 19 and 20) are found to

be high, above the WHO prescribed limit of 50ppm. All the three stations are found to be at the upper course of the river where many agricultural activities are intense, which may be the cause of high concentration of nitrates at these stations.

(b) Chemical Characteristics of major ions

The plots of equilines (Figure 3) for both seasons show a marked difference. In dry season, the plot of $\text{Na}^+ + \text{K}^+$ vs Cl^- show that most of the values fall above and on the equiline and suggest that the alkali is balanced by the Chloride ions. The ratio between the $\text{Na}^+ + \text{K}^+$ and total cation is 0.56 and the ratio between the Cl^- and total anion is also found to be 0.52 indicating that most of the alkali ions are balanced by the chlorides. Among the alkalis, Na^+ is dominant and the concentration of potassium is apparently low. The natural source of potassium in water usually originate from the chemical weathering and subsequent dissolution of minerals of local igneous rocks such as feldspars (orthoclase and microcline), mica and sedimentary rocks as well as silicate and clay minerals (Sarin *et al.*, 1989; Ige *et al.*, 2008).

In wet season, the plot of $\text{Na}^+ + \text{K}^+$ vs Cl^- shows that most of the points are below 1:1 lines suggesting that there is excess of Cl^- over $\text{Na}^+ + \text{K}^+$. Also the plot of $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs $\text{HCO}_3^- + \text{SO}_4^{2-}$ shows that most of the points lie well above the 1:1 equiline indicating that the excess chloride ions are balanced by the alkaline earth metal ions. The ratio of $\text{Na}^+ + \text{K}^+$ with TC is 0.45 and that of $\text{Ca}^{2+} + \text{Mg}^{2+}$ with TC is 0.55 which indicates that there is an inversion of ratio during wet season clearly showing the dominance of alkaline earth metal ions over the alkalis. The ratio of $\text{HCO}_3^- + \text{SO}_4^{2-}$ with TA is 0.26 and that of Cl^- with TA is 0.73 indicating that there is an increase in the concentration of chloride ions in wet season. Cl^- ion concentration in groundwater normally arises from three sources viz., ancient seawater entrapped sediments, solution of halite and related minerals in evaporate deposits and solution of dry fallout from the atmosphere especially in the arid region (Walker *et al.*, 1991).

The high concentration of chloride in the study area does not seem to arise from the above factors but it may be caused by anthropogenic activities and percolation of the saline water near estuary which seeps into the groundwater body thereby increasing the chloride content in the groundwater. The leaching of saline residues of the soil by the action of rainwater during wet season may also contribute to the chemical composition of the water.

(c) Water quality

Piper's diagram

The evolution of hydrochemical parameters of groundwater can be illustrated by plotting the concentration of major cations and anions in the piper's diagram as shown in Figure 4. It indicates that most of the groundwater samples analysed during the dry season and wet season fall in the field of Na-Cl, mixed Ca-Mg-Cl types and mixed Ca-Mg-Cl, Na-Cl and Ca-Cl types of water respectively. 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.

Gibbs diagram

The source of the dissolved ions in the groundwater can be understood by Gibbs diagram (Gibbs, 1970). It is a plot of $(\text{Na}^+ + \text{K}^+)/(\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+})$ vs log TDS and $\text{Cl}^-/(\text{Cl}^- + \text{HCO}_3^-)$ vs log TDS and is as depicted in Figure 5. It shows that almost all the samples of dry season and wet season fall at the boundary of rock dominance and evaporation crystallization dominance area. The Gibbs's diagrams suggest that chemical weathering of the rock forming minerals and evaporation are the main processes which contribute the ions to the water. It is interesting to note that during wet season, precipitation has no dominating effect and no point falls on the precipitation dominating area. Anthropogenic activities may also increase the TDS value (Hem, 1991; Karanth, 1997) and the samples tend to fall on evaporation dominance area in the wet season.

Kelley's ratio

Kelley's ratio is used to find whether groundwater is suitable for irrigation or not. Sodium measured against calcium and magnesium was considered by Kelley (1951) for calculating Kelley's ratio. Groundwater having Kelley's ratio more than one (1) is generally considered as unfit for irrigation. Kelley's ratio for dry season varies from 0.7 to 2.2 with mean of 1.2 and for wet season from 0.2 to 2.5 with a mean of 0.9 (Table 1 and 2) indicating that the water is not suitable for irrigation purposes.

Magnesium ratio

Magnesium present in water would adversely affect the soil quality rendering it unfit for cultivation (Chandu *et al.*, 2008). Magnesium ratio with more than 50% can poison the water (Rajmohan and Elango, 2005). Tables 1 and 2 reveal that 30.4% of dry season samples have magnesium ratio more than 50% and 47.8% of wet season samples had magnesium ratio exceeding 50%. This trend indicates that the area is at the verge of losing its fertility.

Wilcox diagram

Wilcox (1948) used % sodium and electrical conductance in evaluating the suitability of groundwater to irrigation. Sodium-percentage determines the ratio of sodium to the total cation viz., sodium, potassium, calcium and magnesium. All concentration values are expressed in equivalents per million in Figure 6.

The results on tables 1 and 2 show that the groundwater near the downstream is good for irrigation and the contamination are found to be high near the upstream (16, 19 and 20). This may be due to the increased anthropogenic activities near the upstream owing to intense settlements and agricultural activities along the bank of the river and various industries located near the river. At many places starting from the middle course to the northern end of the river, the effluents from the industries as well as the domestic sewage are directed into the river. The near stagnancy of the water in this river facilitates long residence time of the pollutants, which leads to the enhanced percolation of ions into the nearby groundwater. Seasonal effect is apparent at stations 16, 19 and 20 wherein the groundwater quality changes from good to permissible in dry season to unsuitable in wet season, as shown in Figure 6, probably due to the action of leaching and surface runoff of the rainwater.

CONCLUSION

The chemical evaluation of groundwater and the effect of the season on ionic budget around the vicinity of Asa River, Ilorin, Nigeria provides the following conclusions:

Seasonal variations of the chemical parameters were evaluated and the order of abundance of the cations was determined to be $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and $\text{Ca}^{2+} > \text{Mg}^{2+}$, Na^+ , K^+ for dry and wet season respectively, and the order of abundance of anions was $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^-$ during the two seasons. During the dry season, the water types are made of NaCl and Mixed CaMgCl whereas the wet season is constituted by CaMgCl, NaCl and CaCl water type. Total Dissolved Solid values in both seasons (except in some places) were found to be higher than the permissible limit and the concentrations of major ions were higher in the case of wet season indicating leaching and anthropogenic activities predominating over dilution of the groundwater. This was also indicated by the excess Chloride ion over alkalis in the wet season.

Values obtained from Kelley's and Magnesium ratios are higher than those recommended for water suitability for irrigation. Also, Wilcox diagram shows that majority of the water samples are not suitable for irrigation purpose. Hence, water resources in the area could pose danger for irrigation application. Also, Gibbs' diagrams show that the composition of water during both seasons is dominated by evaporation crystallization origin.

Table 1: Summary of the statistical analysis of data (Dry Season).

Parameters (mg/l)	Dry Season			
	Minimum	Maximum	Mean	σ
pH	6.0	6.7	6.3	0.03
EC ($\mu\text{S/cm}$)	1,679.7	5,120.3	2,708.0	1,126.5
TDS	1,075.0	3,277.0	1,733.1	720.0
Ca^{2+}	56.0	208.0	125.0	35.8
Mg^{2+}	16.4	120.6	55.6	32.3
Na^+	136.3	795.0	312.0	193.5
K^+	0.00	44.2	13.0	13.8
HCO_3^-	224.8	1,037.0	375.5	210.5
SO_4^{2-}	204.0	292.0	238.6	30.3
Cl	110.0	1,210.0	435.4	268.8
F	0.5	2.03	1.2	0.4
NO_3^-	4.2	46.0	18.7	11.2
NO_2^-	0.01	1.07	0.3	0.2
PO_4^{3-}	0.2	4.7	1.1	1.1
Gibbs ratio (Cations)	0.5	0.9	0.6	0.1
Gibbs ratio (Anions)	0.4	0.9	0.6	0.1
Kelley.s ratio	0.7	2.2	1.2	0.5
%Na	6.8	84.9	45.2	21.9
Magnesium ratio	13.2	70.6	40.5	15.9

 σ = Std. Deviation

Table 2: Summary of the statistical analysis of data (Wet Season)

Parameters (mg/l)	Wet Season					R (for both season)
	Minimum	Maximum	Mean	σ	t test	
pH	7.5	8.9	8.3	0.4	27.5	S
EC ($\mu\text{S}/\text{cm}$)	656.3	13,759.4	3,558.2	3,031.4	1.7	N
TDS	420.0	8,806.0	2,277.2	1,940.1	1.7	N
Ca^{2+}	48.0	424.0	197.7	114.4	3.1	S
Mg^{2+}	12.0	686.0	134.12	142.5	3.0	S
Na^+	31.8	1,120.0	391.3	331.14	1.6	N
K^+	0.00	64.8	11.3	17.6	0.7	N
HCO_3^-	170.8	732.0	368.9	148.2	0.2	N
SO_4^{2-}	32.4	272.0	176.7	68.27	4.9	S
Cl ⁻	150.0	3,470.0	956.9	903.2	3.1	S
F ⁻	0.2	0.9	0.5	0.2	1.1	N
NO_3^-	1.02	75.9	21.1	22.2	0.5	N
NO_2^-	0.1	3.6	0.7	1.03	2.0	N
PO_4^{3-}	0	0.1	0.06	0.03	1.05	N
Gibbs ratio (Cations)	0.4	0.9	0.6	0.1	2.3	S
Gibbs ratio (Anions)	0.5	0.9	0.8	0.12	3.2	S
Kelley.s ratio	0.2	2.5	0.9	0.5	2.8	S
%Na	17.0	70.8	42.8	12.7	0.4	N
Magnesium Ratio	17.5	74.8	47.0	16.1	1.9	N

R= Remark, S= Significant, N= Non- Significant, σ = Std. Deviation

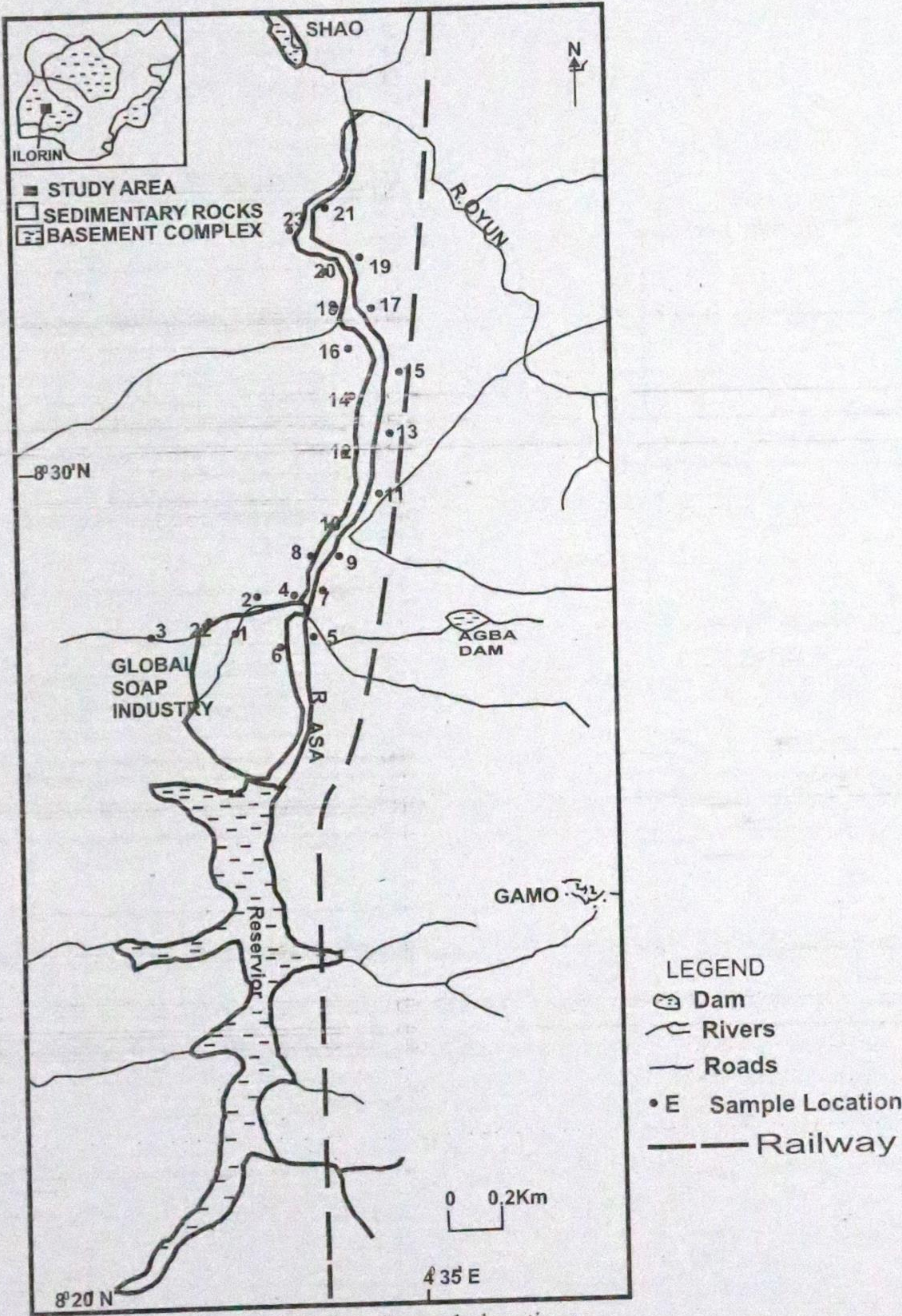


Figure 1: The Asa River and sample locations
(Modified from Olasehinde *et al.*, 1998)

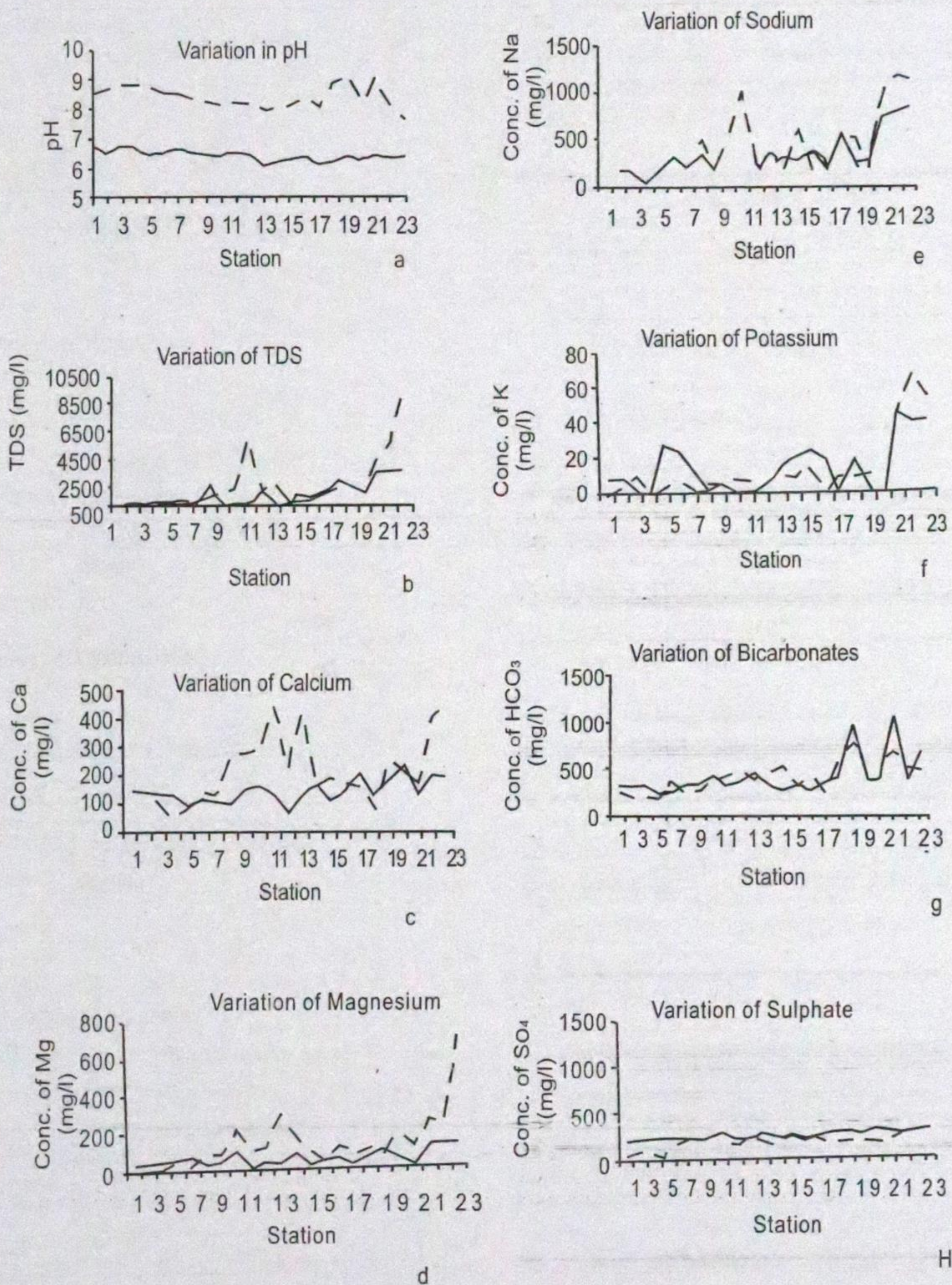


Figure 2: Seasonal variation of the chemical parameters

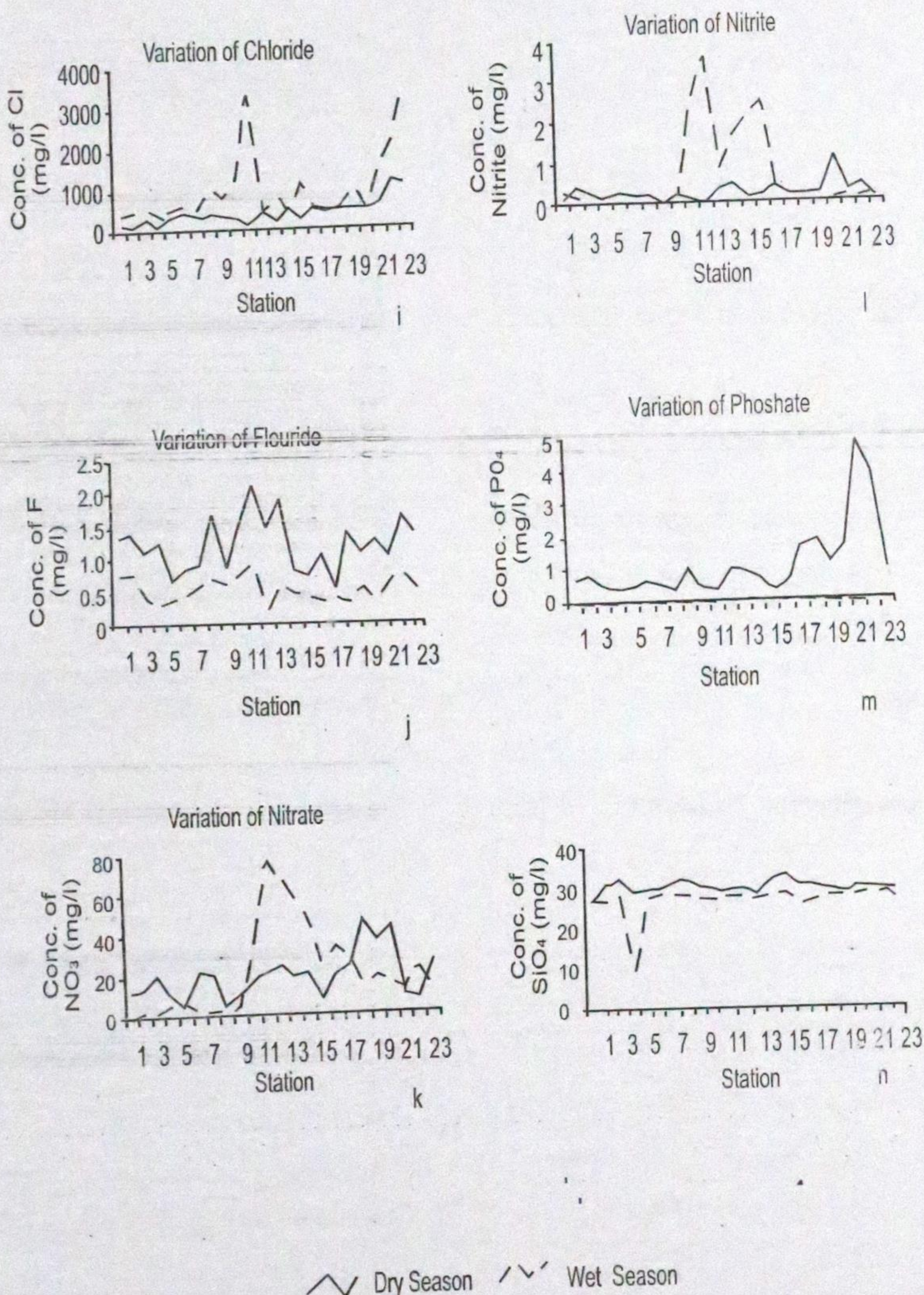


Figure 2 (continued)

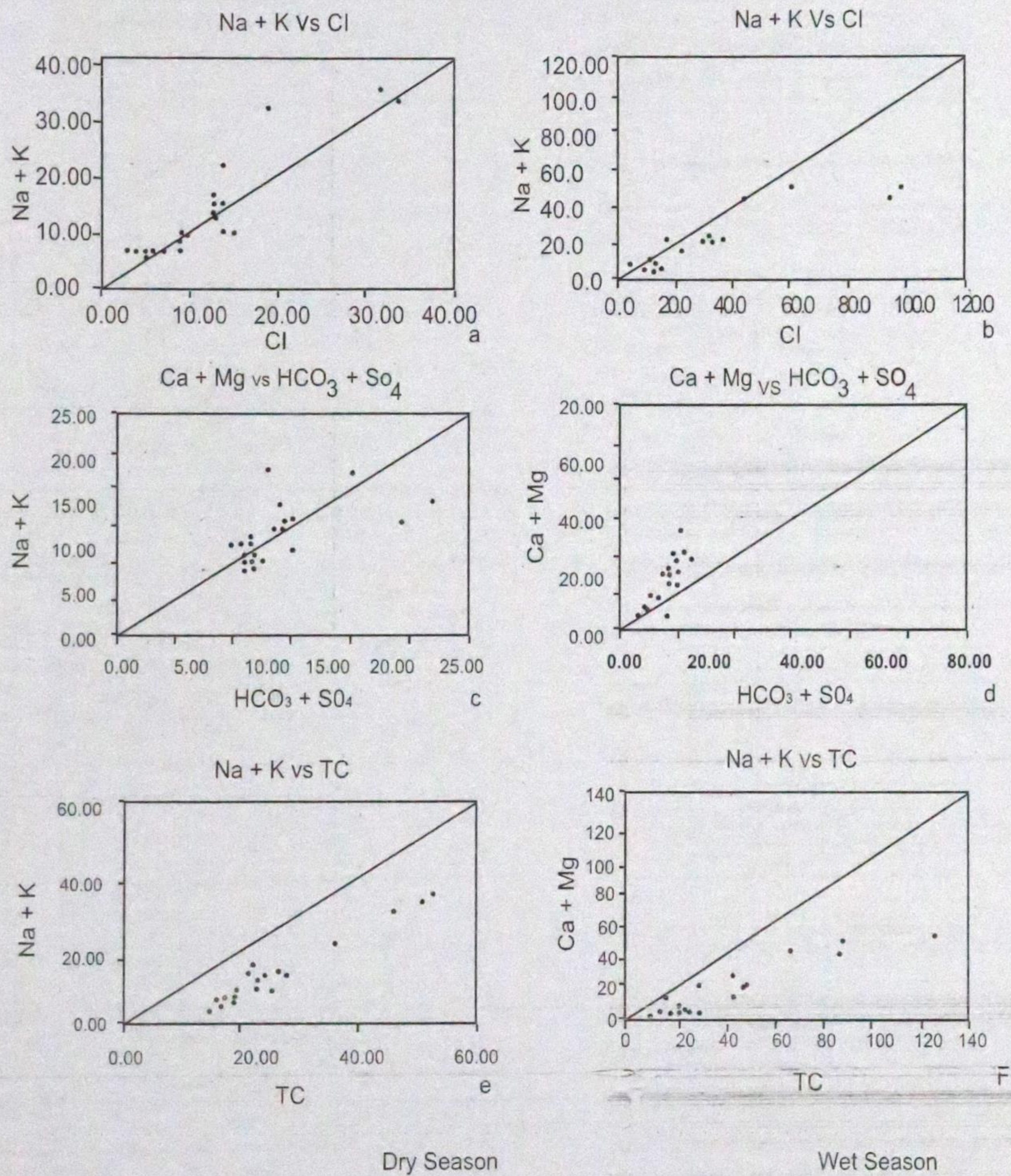


Figure 3 Equiline diagrams

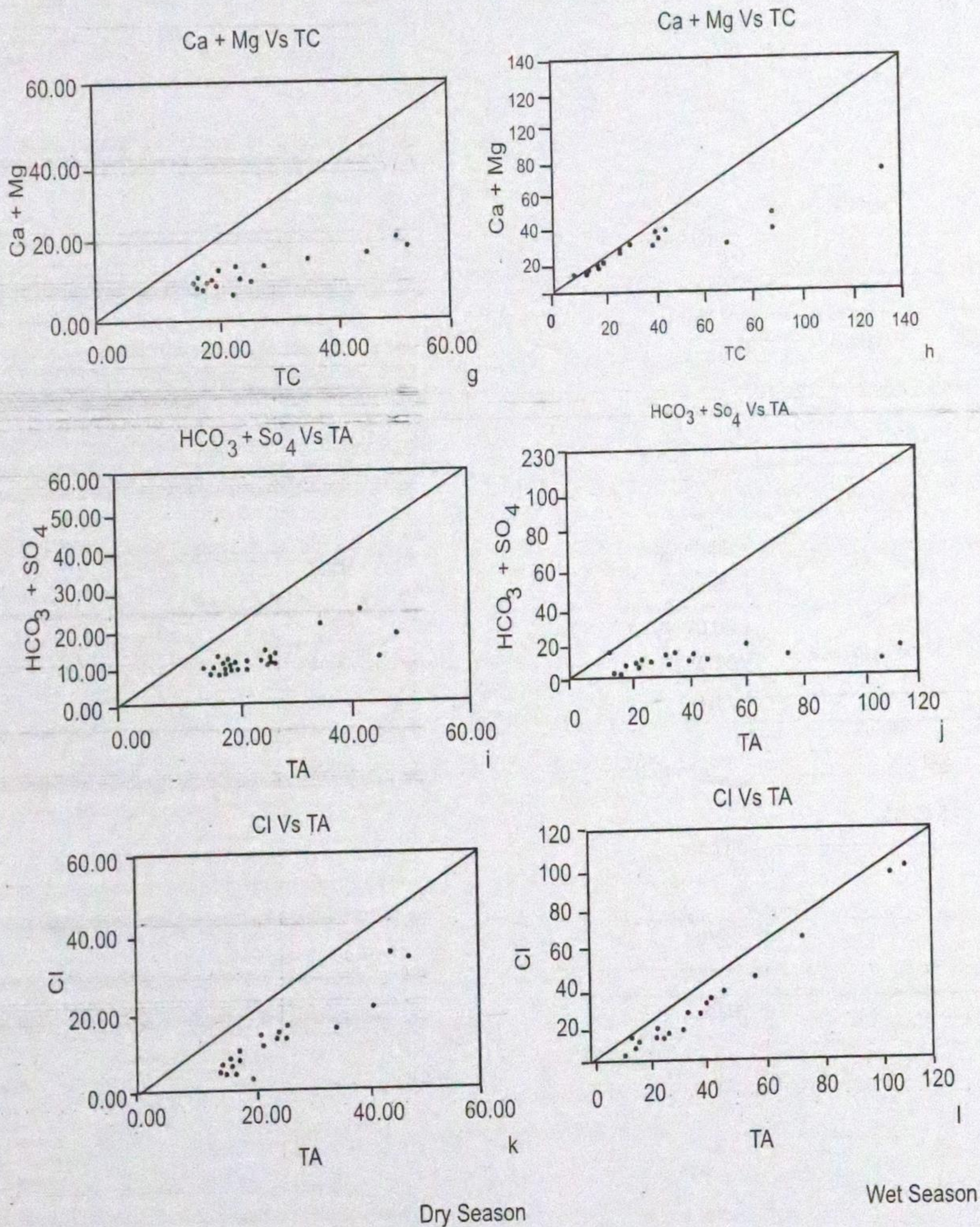


Figure 3 (Continued)

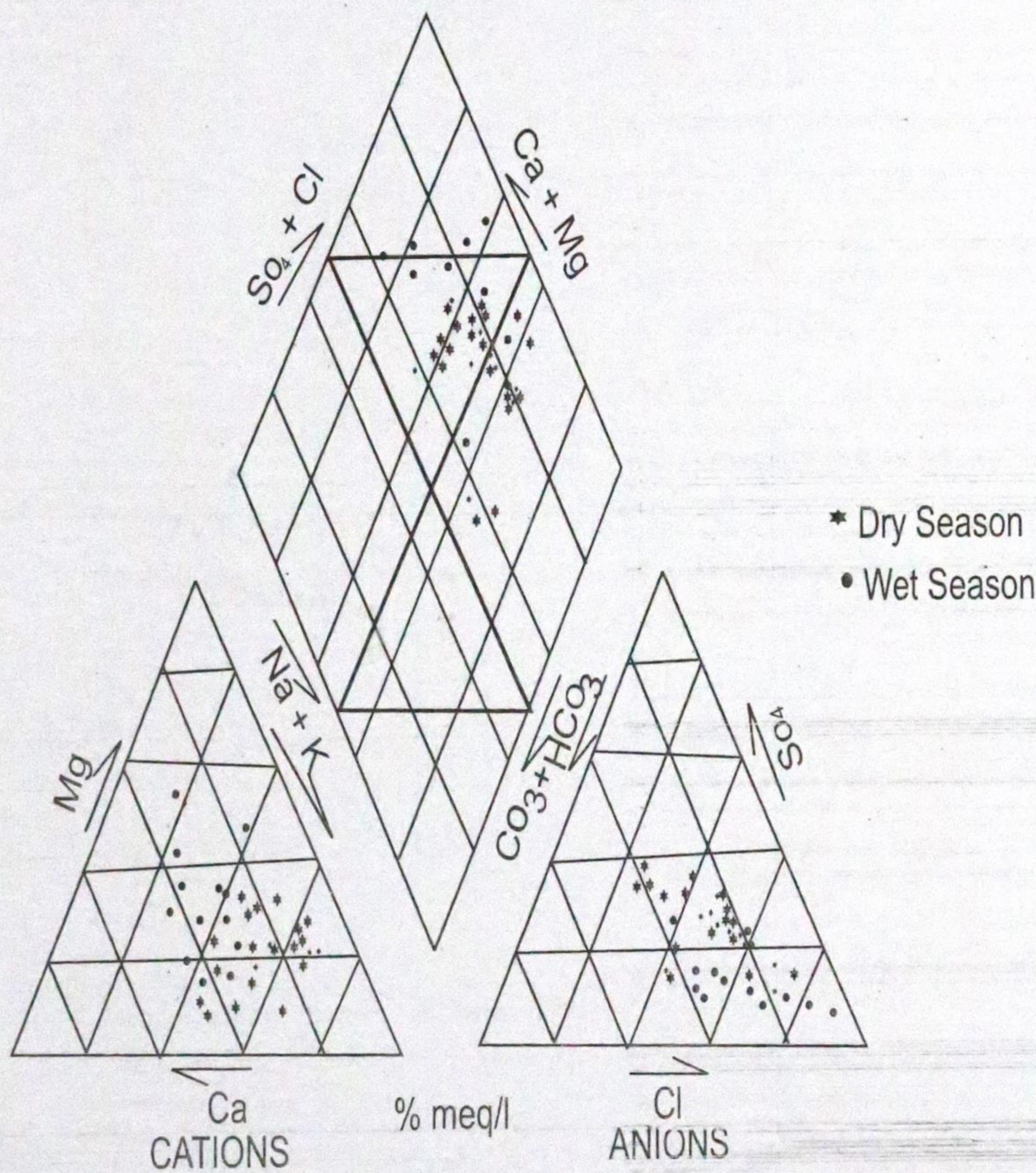


Figure 4: The Positions of the water samples on the Piper's diagram

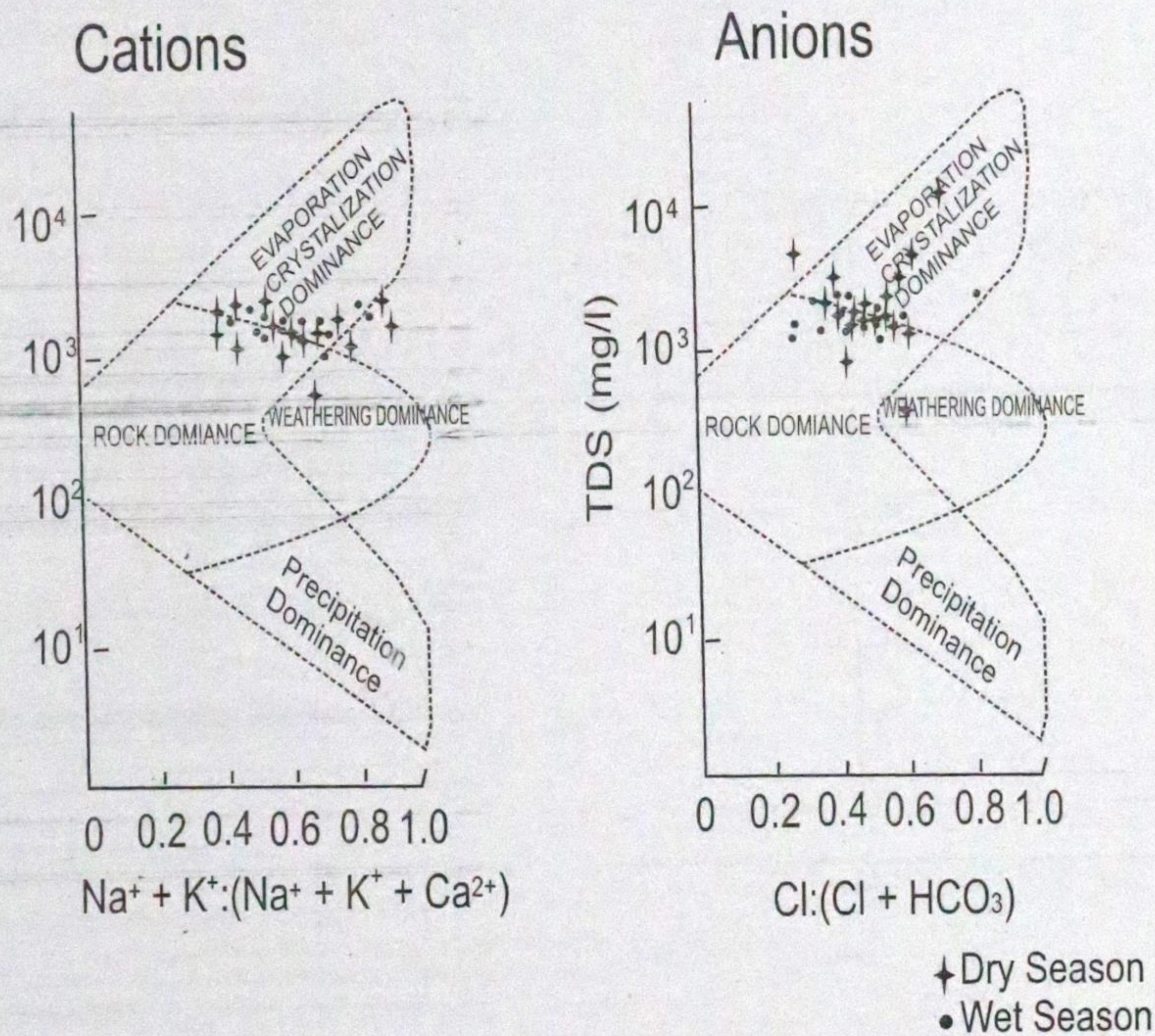


Fig. 5: The Positions of the water samples on the Gibbs' diagrams

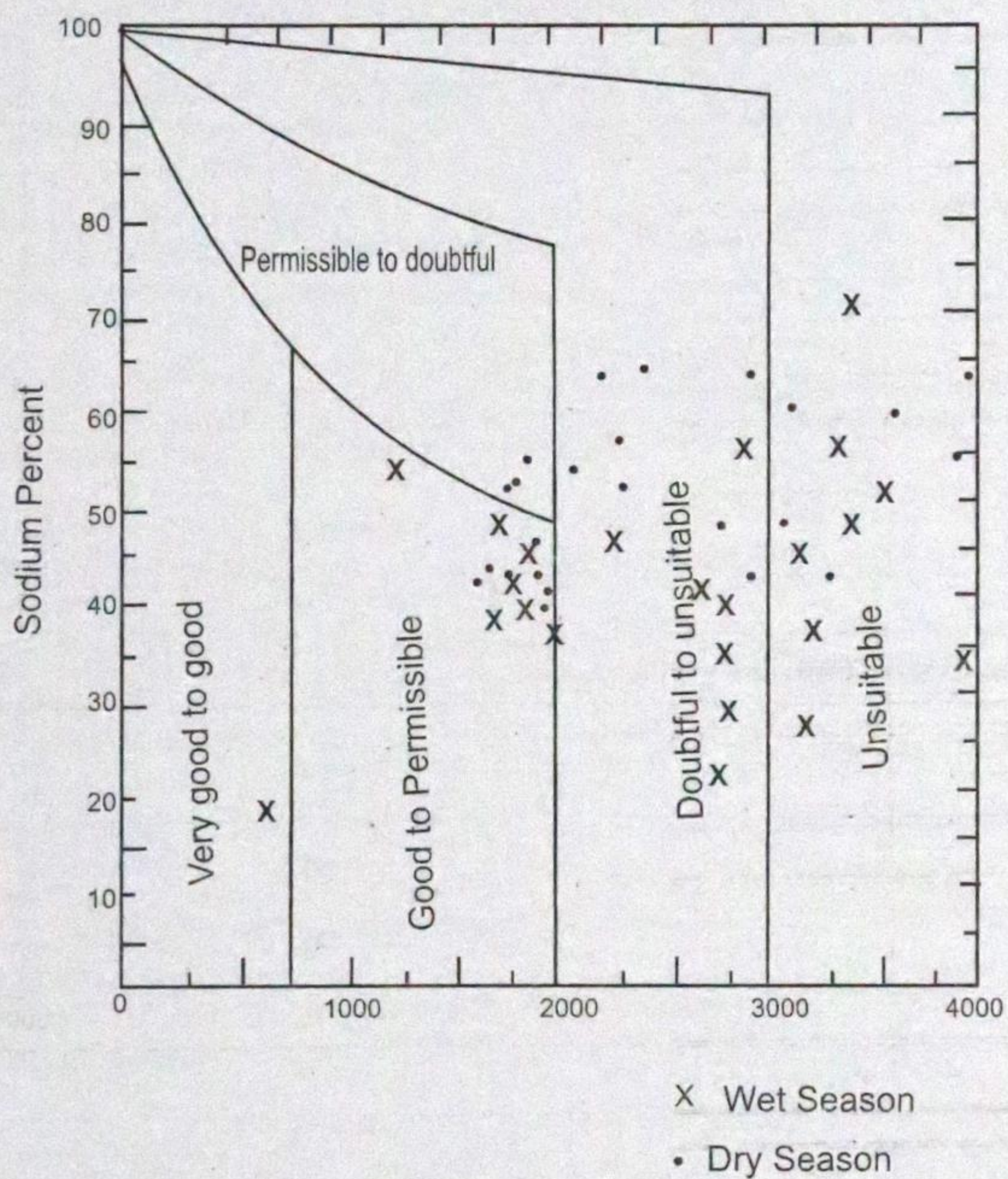


Figure 6: Position of the water samples on the Percentage of sodium and conductance relationship for rating irrigation water (Wilcox,1948)

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