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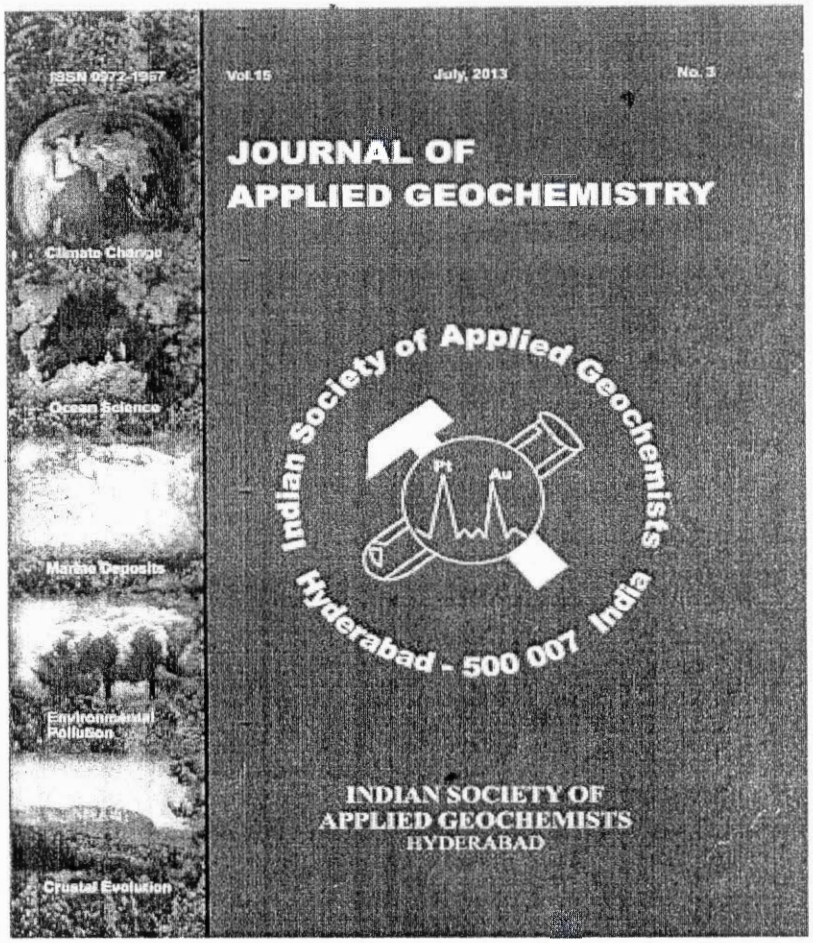

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GEOCHEMICAL DISTRIBUTION OF GROUNDWATER WITHIN AND AROUND AGO IWOYE, SOUTHWEST NIGERIA.

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Abstract

The need for assessment of suitability of groundwater resources for drinking and irrigation purposes become pertinent in the face of continuous increasing global pollution threats of groundwater. This work assesses the physical and chemical characteristics of the local groundwater resources around Ago Iwoye, southwest, Nigeria, to determine its suitability for drinking and irrigation. Results showed that water samples have generally low total dissolved solids with range values of 90-534mg/L, pH ranges from 4-7.9 while total hardness varies from 20-221 mg/L $CaCO_3$ soft to slightly hard. Ranges of the concentrations of cations for the study area were 1.5-26.5Mg/l, 1.3-15.8Mg/l, 6-58.1Mg/l and 1.8Mg/l for Ca, Mg, Na and K respectively while anion showed ranges of 35-161Mg/l, 24-1463Mg/l and 1.0-36.8Mg/l for HCO_3, Cl and SO_4 respectively.

All the water samples in the study area based on cations and anions fall within safer zone for drinking and irrigation purposes except for Cl and HCO_3 which showed higher values in 10% and 35% of water respectively. The results of Sodium Absorption Ratio (SAR), Magnesium Absorption ratio (MAR), Permeability Index (PI), Soluble Sodium Percentage (SSP), Residual Sodium Bicarbonate (RSBC), and Kelly ratio (KR) range between 2.15-14.43, 10.49-86.9%, 1.15-22.57%, 28.8-72.02%, 2.1-2.41 and 0.41-2.41% respectively. All the water samples are excellent for irrigation with regards to all the parameters except MAR and KR which showed hazard in 30% and 50 % of water respectively.

All the trace elements analyzed have values below the recommended standard limit except barium in only one sample with value of 0.909mg/l. The values of pollution index for all sites fall below 1 which confirmed suitability of most of the water samples for both drinking and irrigation purposes. This work showed that the geology appears to have greater influence on the chemical transformation of the groundwater resources especially major elements, compared to any possible effects due to the anthropogenic activities.

Keywords: Water; Quality; Irrigation; Geochemistry; Pollution

1. Introduction

Water plays an important role for the existence and sustenance of life. It is indispensable and utilized in essential activities including human consumption, agriculture, industry, transportation, hydro-electric power generation and recreation. One of the most important crises of the twenty first century is the scarcity of drinking water. Most freshwater bodies of the world over are becoming increasingly polluted, thus affecting the quality of water and approximately 97% of the earth's useable fresh water is stored as groundwater. Groundwater can be contaminated by lack of sanitation, uncontrolled applications of fertilizers and manure, as well as indiscriminate disposal of domestic wastes. Rapid urbanization, especially in developing countries like Nigeria, has also affected the availability and quality of groundwater. 80% of all the diseases in human being are water-borne according to world health organization and once groundwater is polluted, its quality cannot be restored by stopping the pollutants from the source. Consumption of water with high concentration of major and trace elements has been reported to cause

disorders of alimentary canal, respiratory, nervous and coronary systems as well as miscarriage and cancer. Crops irrigated with such groundwater also show poor seed germination, retardation and development. It therefore becomes important to regularly monitor the quality of groundwater to ensure its suitability for drinking and irrigation purposes and to protect it. Hence, this work intends to assess the physico-chemical characteristics of groundwater resources within Ago Iwoye, Southwest Nigeria and its environs in order to determine its suitability for drinking and irrigation purposes.

2. Description of the study area

The study area which comprises of Ago Iwoye is within Basement complex of the Southwestern Nigeria, occurs between Precambrian to lower Paleozoic (Jones and Hockey, 1964, Rahaman 1976). It is located in latitude 06"56' to 07 00'N and longitude 03"56' to 04"00'E. There are two distinct seasons namely the rainy season (April – October) and the dry season (November – March) within the area. The rainy season is characterized by high rainfall with an average annual rainfall of 750 - 1000mm (Olayinka, et al., 2000), while the dry season is characterized by dry, dust-laden wind. The natural vegetation consists of multitudes of evergreen trees ranging from tropical hardwood, palm trees and green grasses. Different types of crops are cultivated which include cocoyam, maize, cassava, yam, cocoa and others. Occupation of the people in this area is farming and many people engage in different crop plantation. There are also two different lumbering sites in this area. The drainage pattern is dendritic.

The geology of the study area lies within Basement complex of Nigeria which consists of crystalline igneous and metamorphic rocks. The rocks are either directly exposed or covered by shallow mantle of sand and clay. The complex is an extension of the Togo – Benin – Nigeria shield which occur East of West African Craton. The rocks in the study area consist of granites, minor amphibolites, schist, quartzite, pegmatite, migmatite and gneiss with minor intrusions. The igneous and metamorphic rocks of the Basement Complex are crystalline in nature and have low porosity and permeability. Therefore, the aquifer units in the study area are found in weathered rocks and are probably enhanced by the presence of the observed structural features. The major source of water supply within the area is through the shallow hand-dug wells which can easily be contaminated by anthropogenic activities such as indiscriminate dumping of solid wastes and sewage activities.

3. Methodology

Twenty samples of groundwater drawn from hand dug wells and boreholes were collected locations within Ago Iwoye and its environs Fig. 1. Several sensitive parameters of water such as Total Dissolved Solids (TDS), Electrical Conductivity (EC) and pH were determined in the field using the appropriate digital meters (e.g. water treatment works (WTW)-conductivity meter model LF92 and WTW-pH meter model pH/91).

The analysis of trace elements and cations in water were carried out using inductively coupled plasma optical emission spectrometry (ICP-OES) while acidified water samples were analyzed for anions concentrations using the DIONEX DX-120 ion chromatography techniques. All analyses were carried out at the ACME laboratory, Ontario Canada.

To check the accuracy, activation laboratories (Ontario, Canada) employed two internal standards (each run twice) and found that the errors were consistently minimal.

Samples from all the water samples were analyzed for 73 constituents and physical properties.

More than three quarter (62) of the 73 constituents analyzed for were not detected above the laboratory reporting levels (LRLs) in any sample. The summaries which include range, mean, standard deviation

Table1. Summary of Physico-chemical parameters in water samples

Parameters	Min	Max	Average	St. deviation	WHO, 2010 Standard
PH	4	7.8	6.29	1.4	6.5-8.5
TDS	92	605	276.25	185.86	500
Ca	1.5	26.5	16.305	6.19	
Mg	1.3	15.8	7.96	4.78	
Na	6	48.4	25.27	11.98	200
K	1	8	3.93	2.02	
SO4	1.69	36.8	11.28	41.43	250
Cl	24	1463	118.84	303.27	250
HCO3	35	161	95.85	35.83	
B	5	24	7.45	4.65	
Ba	52.44	909.62	176.09	219.96	700
Cr	1.5	14.4	6.84	4.99	100
Cu	0.5	8.7	2.31	2.55	1000
Mn	0.05	356.55	47.14	78.32	400
Ni	0.2	0.4	0.25	0.076	20
Pb	0.1	9.4	0.81	2.06	10
Sb	0.22	92	15.61	26.52	20
U	0.02	0.35	0.06	0.08	
Zn	0.9	QAXC	18.78	34.96	3000
Ce	0.09	4.75	1.2	1.42	
Co	0.27	85	14.88	24.24	
Li	0.2	15.5	2.9	3.61	
Tl	0.01	0.02	0.013	0.006	
V	9.5	10.7	2.45	3.17	

4.2 Chemical characteristics of water

Calcium ranges from 1.5 to 26.5mg/l with an average of 16.31(Table 1). Ca concentration in all water samples are <40mg/l and can be classified as good groundwater zones based on WHO (2010) Table. 4. Mg ranges from 1.3 to 16.5mg/l with an average of 7.98. (Table1). Probable release of magnesium might be from biotite granites and biotite

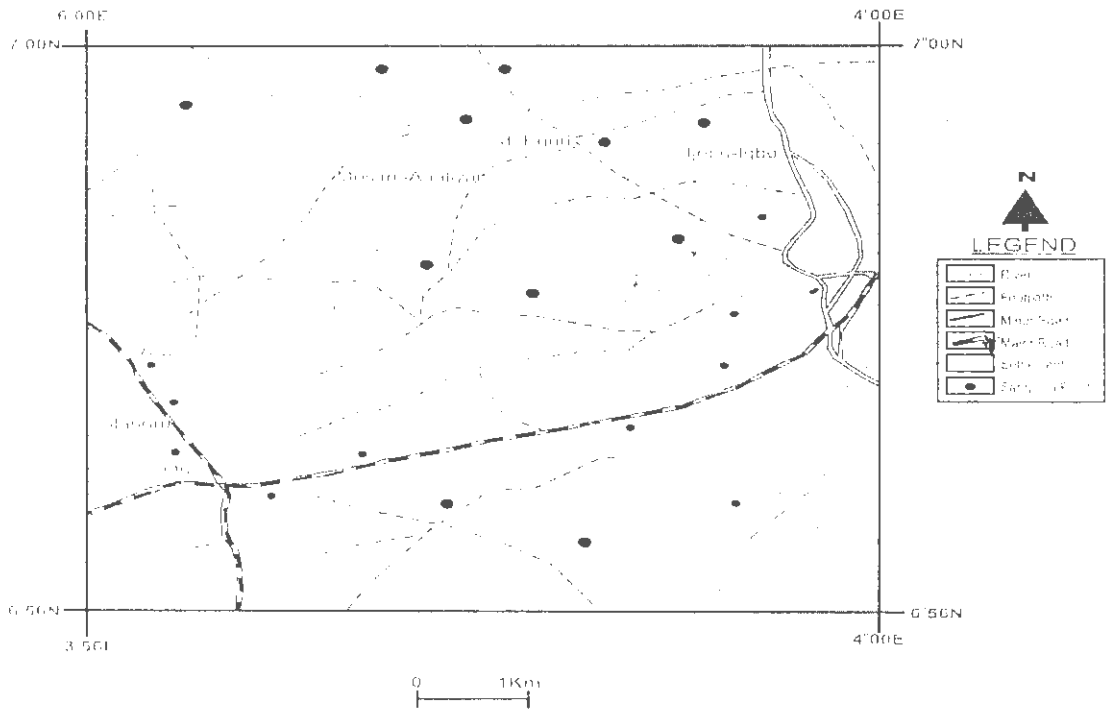

Fig. 1 Map showing sample locations

were presented in Table. 1 for physical and major elements and trace elements. Analytical results for significant elements were compared with World Health Organisation WHO 2010 standard. Parameters such as Sodium Adsorption Ratio (SAR), Soluble Sodium Percentage (SSP), Residual Sodium Bicarbonate (RSBC), Magnesium Adsorption Ratio (MAR), Kellys Ratio (KR) and Permeability Index (PI) were also calculated from the result to determine the suitability of water for irrigation purpose using the equation in Oladejo et al 2012. Results were also further compared with recommended standards and pollution index was calculated to determine the water quality for human consumption.

4. Results and Discussion

4.1 Physical Properties

The summary of the physical parameters, cations, anions and trace elements determined from the water samples are presented in Table 1. The pH ranges from 4.00 to 7.90; the mean is 6.29 (Table. 1). Low pH value of less than 8 are said to be an indication of the presence of free CO_2 and that the dissolved carbonates exist almost entirely as HCO_3 ion form. Also based on the classification by Ezeigbo, (1989) the water samples vary between acidic to slightly alkaline. 50% of the samples were acidic and fall out of World Health Organization Standard (WHO, 2010). Total Dissolved Solids (TDS) and Total hardness of the samples range from 92 - 793mg/l and 20 -221mg/l$CaCO_3$ respectively. All the water samples except the ones at locations 1, 7 and 8 can be classified as fresh water and are within the recommended standards of 500mg/l for TDS (WHO, 2010). The water can also be classified as excellent and fair for irrigation purpose Table. 2. Total Hardness (TH) indicates that the water in the study area is between soft to slightly hard (Table. 3.)

Table. 2. Classification of Water Based on TDS (Todd, 1980)

<1000	Fresh
1000-3000	Slightly Saline
3000-10000	Moderately Saline
10000-35000	Very Saline
>35000	Brine

Table. 3. Classification of Hardness by (TODD, 1980)

0-60	Soft
61-120	Moderately Hard
121-180	Hard
>180	Very Hard

gneiss from the study area. Magnesium concentration is classified with less than 30mg/l as a safer zone for drinking water (Table. 5). All water samples in the study area fall within safer zone for drinking purposes. Na and K range from 6-48.4mg/l and 1.8mg/l with mean values of 25.27 and 3.93 respectively. Na is the most dominant cation in the study area. Presence of sodium and potassium is attributed to the primary source of weathering of alkali feldspar. High weathering of feldspathic gneiss along the gneissic terrain indicates alkali

Table. 4. Classification of Calcium

Concentration of Calcium	Suitable Zones
<40mg/l	Good
40-70mg/l	Moderate
>70mg/l	Poor

Table. 5. Classification of Magnesium

Concentration of Magnesium	Suitable Zones
<30mg/l	Good
30-120mg/l	Moderate
>120mg/l	Poor

concentration in the study area. All samples can be categorized based on (WHO, 2010) standard as suitable for drinking water (< 100 mg/l) (Table. 6). High concentration of Na has been linked to heart diseases. The cations in the water samples follow the trend Na> Ca> Mg> K.

Bicarbonate ranges between 35 to 161mg/l with the mean value of 95.85. Primary source of bicarbonate ions in groundwater is the dissolved CO_2 in rain water, which when enters the soil dissolves more carbon-dioxide. Decay of organic

Table. 6. Classification of Sulphate

Concentration of Sulphate	Suitable Zones
<200mg/l	Good
200-400mg/l	Moderate
>400mg/l	Poor

matter and SO_2 reducing bacteria may also release CO_2 for dissolution. Water charged with CO_2 dissolve carbonate minerals, which passes through soil and rocks to give bicarbonates. The concentration 65% of the samples were <100mg/l and good for irrigation and drinking according to the classification based on WHO standard while 35% of the samples showed value > 100 ppm and categorized as moderate zone which is suitable for industrial activity but not good for drinking puposes (Table. 7).

Chloride water samples in the study area are below 100mg/l except for two samples which contain higher concentration (> 1000 mg/l) of Cl^-. Chloride ion occurs in natural water in fairly low

Table. 7. Classification of Alkalies

Concentration of Sodium	Suitable Zones
< 100mg/l	Good
100-500mg/l	Moderate
>500mg/l	Poor

concentrations, usually less than 100 mg/l , unless the water is brackish or saline. All water samples can be classified as good suitable zones except for two samples that fall within moderately suitable zones and poor zones (Table 8). Sulphate concentration ranges between 2.6 to 36.8mg/l. All samples fall within good zone for drinking based on WHO standard (Table 9). The anions follow the trend, $Cl>HCO_3>SO_4$.

4.3 Hydrogeochemical processes

The ratios between Total cations and Na+K as well as Ca+Mg are 0.89 and 0.48 respectively (Fig 2). This observation showed the involvement of

Table. 8. Classification of Chloride

Concentration of Chloride	Suitable Zones
< 100mg/l	Good
100-250mg/l	Moderate
>250mg/l	Poor

Table. 9. Classification of Bicarbonate

Concentration of Bicarbonate	Suitable Zones
< 100mg/l	Good
100-250mg/l	Moderate
>250mg/l	Poor

silicate weathering in the geochemical processes, which contribute mainly sodium, calcium and potassium ions to the groundwater (Stallard and Edmond 1983; Sarin et al. 1989). Weathering of soda feldspar (albite) and potash feldspars (orthoclase and microcline), which are common in granites, gneiss and pegmatite occurring in this area is greatly responsible for the contribution of Na^+ and K^+ ions to groundwater. Feldspars are more susceptible for weathering and alteration than quartz in silicate rocks. The regional geology also implies that the alkali earth silicates occur everywhere in the area.

4.4 Ion exchange

Ion exchange is one of the important processes responsible for the concentration of ions in groundwater is ion exchange. Chloro-alkaline indices (CAI and CA2) calculated for the groundwater samples of the study area strongly suggest the occurrence of ion exchange process.

$CAI = Cl^- - (Na^+ + K^+)/Cl^-$

$CAI\,2 - Cl^- - Na^+ + K^+ - SO_4^{2-} + HCO_3^- + CO_3^{2-} + NO_3^-$

(All values are expressed in meq /l).

When there is an exchange between Ca or Mg in the groundwater with Na and K in the aquifer material, the above index is negative, and if there is a reverse ion exchange, then the index will be positive (Schoeller 1965, 1967). CAI and CA2 values of the study area range between -6.05-39.47 and -0.41-38.71 (Fig. 3). This observation indicates that reverse ion exchange is the dominant process in the groundwater (75% and 85%), whereas normal ion exchange is also noticed in water samples.

4.5 Trace Elements

All the trace elements analyzed have values below the recommended standard except barium in only one sample with value of 909mg/l. The average trace element concentration in the surface water samples of the study area is given in (Table. 1).

The concentrations of Ba, Mn, Cr, Ni and Co are as follows 52.44 to 909.62mg/l, 0.05 to 356.55mg/l, 1.5mgll to 14.4mgll, 0.2mg/l to 0.43 mg/l and 0.27 to 85 mg/l with the following averages

176.09, 47.14, 6.84, 0.25 and 14.88 respectively. Cu, Pb, Sb, Cr, Zn, Ce, Li, Tl, and V have the following mean values 2.31, 0.81, 15.61, 0.06, 18.78, 1.2, 2.9, 0.013 and 7.45 respectively. All the trace elements are within WHO, 2010 standard except Ba in one sample and Sb in four samples. The plots of significant trace elements against total cations showed very low correlation (Fig. 4) which indicates probability of different sources. Major elements are probably from weathering of the bedrocks in the study area while trace elements may be from the anthropogenic sources.

6. Water Suitability for Irrigation Purpose

6.1 Sodium Adsorption Ratio (SAR)

Sodium Adsorption Ratio (SAR = Na / (Na + Ca+/2) the water samples range from 2.15 to 14.43 and can be classified as excellent and good for irrigation Table. 10 (Todd, 1980). Approximately 80% of the values obtained for the Sodium Adsorption Ratio (SAR) during the present study are generally less than 10 and can be classified as excellent while the remaining 20% can be classified as good for the purpose of irrigation.

6.2 Magnesium Absorption Ratio (MAR)

The range of values obtained for the Magnesium Adsorption Ratio (MAR) of the water samples between 10.49 and 80.9%. Magnesium content of water is considered as one of the most important qualitative criteria in determining the quality of water for irrigation. Generally, calcium and magnesium maintain a state of equilibrium in most waters, but increasing amount of magnesium in water will increase the salinity of the water and Based on the MAR values, 70% of the waters are considered suitable with no hazardous effects to the soil Table 10

6.3 Permeability Index

The values of the Permeability Index obtained in this work ranges between 4.15% - 22.57 %. Generally, the soil permeability is affected by the long term use of irrigated water with high

Table 10: Characteristics of Water for Irrigation Purpose

SAR	SSP	RSBC	PI	MAR	KR
9.43	67.65	0.86	39.81	52.05	1.93
13.37	65.34	1.05	66.18	64.33	1.85
2.23	36.96	1.61	16.02	11.15	0.41
14.43	74.02	0.89	139	1116.5	2.41
7.19	66.76	0.93	33.04	44.51	1.44
9.12	63.37	2.41	47.98	53.03	1.37
10.61	59.07	1.35	70.73	131.91	1.29
2.15	28.8	0.06	12.21	10.49	0.32
3.94	33.02	0.39	30.25	46.78	0.46
4.11	38.55	0.33	27.21	33.34	0.51
6.83	53.02	0.99	37.7	41.49	0.94
4.99	46.79	1.17	31.11	52.45	0.75
13.4	61.88	2.16	71.77	123.28	1.46
8.15	60.76	1.26	37.52	35.78	1.38
8.76	57.79	1.36	43.98	33.05	1.22
5.95	50	1.05	32.57	38.08	0.87
6.5	55.39	1.49	32.14	30.19	1.08
6.41	53	1.3	41.63	93.36	0.95
4.97	40.58	2.01	36.06	47.19	0.6
6.92	50	-0.51	46.42	75.5	0.85

values of total dissolved solids and sodium bicarbonate. However, based on the classification presented by (Doneen, 1964), the results obtained in this work fall within the Class I category, which is described as excellent irrigation water.

6.4 Soluble Sodium Percentage (SSP)

Soluble Sodium Percentage (SSP) parameter provides an estimate of the percentage of sodium ions present in the water sample, which

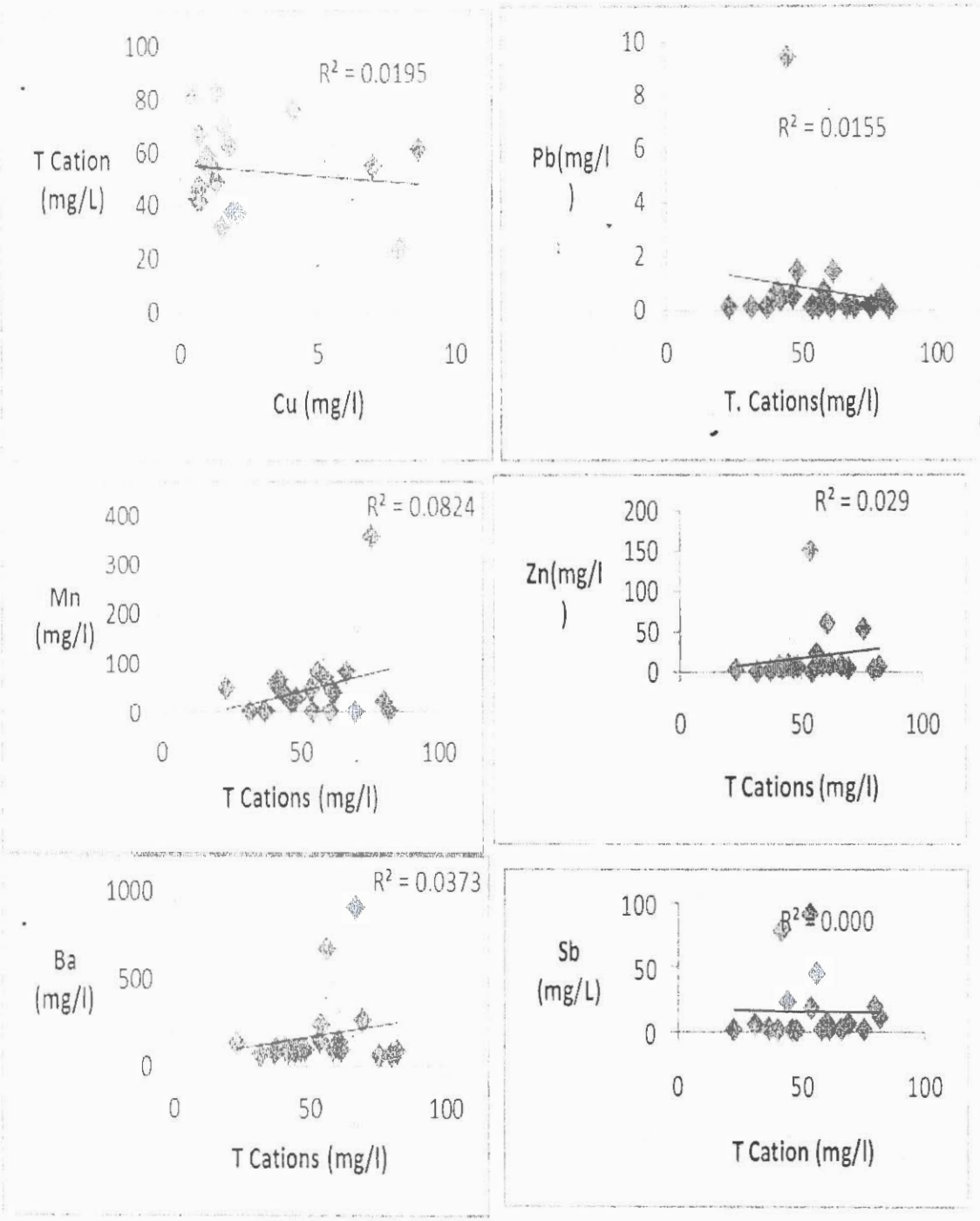

Fig. 4. Plots of Total Cations against Trace elements

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further provides an indication of the probable hazard that could be resulted from accumulation of sodium ions. Therefore, SSP is frequently used in the determination of the suitability of water for irrigation purpose. According to (Joshi et. al., 2009), a high percentage of sodium in the water for irrigation purpose can potentially stunt the plant growth and reduces soil permeability. In this work, the values obtained for the SSP parameter range between 28.8 and 72.02%. According to (Wilcox, 1948) All SSP values obtained in the present work are within the recommended permissible limit of 80%, and therefore these water samples (W1 – W10) are classified as 'excellent' for the purpose of irrigation.

Residual Sodium Bicarbonate (RSBC) values obtained for the water samples vary between -2.1 to 2.41 meq/L. Generally, the concentration of bicarbonate and carbonate within the soil influences the suitability of water for irrigation purpose, because water samples with high RSBC value tend to have relatively high pH values. Therefore land irrigated with such water becomes infertile owing to deposition of sodium carbonate (Eaton, 1950). In this work, the range of values obtained for the RSBC for the water samples is -2.1 to 2.41 meqL^{-1}. Based on the rating indices, these water samples are described as 'Good' for irrigation. Also, the ranges of values for the Kelly's Ratio (KR) obtained for the water samples is 0.41 – 2.41. The values obtained are slightly higher than the permissible limit of 1.0 recommended by Ayers and Westcot (1985) in 50% of the total samples.

6.5 Pollution index

The pollution index was used in this study to evaluate the degree of trace metal contamination (Nishida et al., 1982; Chon, et al., 1991; Kim et al., 1998, Emoyan et al., 2005; Nier, 2007). The tolerable level is the element concentration in the water considered safe for human consumption (Kloke, 1979; Lee et al., 1998). The (WHO, 2010) standard was used as tolerable level for water and the pollution index can be calculated using the formula below.

$$PI = \frac{\text{Heavy metal concentration in water}}{\text{Tolerable level}} \Big/ \text{Number of heavy metals}$$

The results of Pollution Index for all the water samples are below 1 which indicate no contamination with regards to trace elements.

Conclusion

The groundwater quality of Ago Iwoye, Southwest Nigeria was assessed for its drinking and irrigational suitability. Results showed that water samples have generally low total dissolved solids with average values of 90-534mg/l. pH ranges from 4-7.9 while total hardness varies from 20-221 mg/L $CaCO_3$ (soft to slightly hard). Average concentrations of cations for the study area were 16.31, 7.98, 25.27 and 3.93 for Ca, Mg, Na and K respectively while anion showed average concentrations of 95.85, 118.84 and 36.8 for HCO_3, Cl and SO_4 respectively.

All the water samples in the study area based on cations and anions fall within safer zone for drinking and irrigation purposes except for Cl and HCO_3 which showed higher values in 10% and 35% of water samples respectively.

The values of Total Dissolved Solids (92 – 276.25 mg/l), Potassium ratio (KR) (0.41-2.41), Soluble Sodium Percentage (28.8 - 72.02), Permeability Index (4.15 - 22.57 %), Residual Sodium Bicarbonate (-2.1 – 2.41) and Sodium Adsorption Ratio (2.15-14.43). Magnesium Absorption ratio (MAR) 10.49-86.9 indicate that the water quality was suitable for irrigation purpose. All the trace elements are within (WHO, 2010)

standard except Ba in one sample and Sb in four samples while Pollution index is below 1 for all the samples which showed no contamination. The geology appears to have greater influence on the chemical transformation of the groundwater resources, compared to any possible effects due to the anthropogenic activities within the study area.

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