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PHYSICOCHEMICAL QUALITY, POTENTIALLY TOXIC ELEMENTS CHARACTERIZATION INVESTIGATION OF SEASONAL CHANGES IN QUALITY PARAMETERS OF LADOKUN RIVER WATER AND ITS FITNESS FOR IRRIGATION PURPOSES

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ABSTRACT

In the present investigation an attempt was made for the assessment of Ladokun river water fitness for irrigation purpose. Samples of Ladokun river water were collected during the dry and wet seasons and data gotten were analyzed for various parameters. The results indicated that total dissolved solids (TDS), electrical conductivity (EC), potassium (K^+), sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), phosphate (PO_3-P), sulphate (SO_4^{2-}), nitrate (NO_3-N) and bicarbonate (HCO_3^-) were within the recommended limits set for irrigation water standard, however, the hydrogen potential(pH) range was slightly acidulous in the dry season but more alkaline during the wet season. The water quality indicators, including magnesium absorption ratio (MAR), soluble sodium percentage (SSP), total hardness (TH), residual sodium carbonate (RSC), sodium adsorption ratio (SAR), permeability Index (PI), potential salinity (PS) and kelly's ratio (KR) were all within safe limits for both seasons. Ultimately, the findings indicate that Ladokun river water is suitable for irrigation purposes, and farmers in the area can use it to grow their crops without ominous effects, although, continuous monitoring of water quality is essential to ensure that it remains within safe limits, and appropriate measures should be taken to address any issues that may spring up.

Keywords - Assessment, Water quality, Irrigation.

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INTRODUCTION

Lakes, streams and rivers are the principal surface water sources that are accessible to human for consumption, irrigation and other uses throughout the world (Ustaoglu *et al.*, 2021; Shil *et al.*, 2019). The knowledge of irrigation water quality is vital to soil conservation and maximum agricultural productivity. Irrigation is an effective way to improve productivity significantly. Moreover, there are environmental hazards associated with irrigation, such as water stagnation, refuse dumping into the river channels, drainage channeled to the river from buildings and animals rearing houses and increased salinity.

Unfortunately, the crop productivity is associated with the quality of soil and the quality of the water available for irrigation. Normally, investigation of irrigation water quality should be based upon salt content, sodium concentration, the occurrence of nutrients, alkalinity, acidity, and hardness of the water. Salinity problem leads to the loss of fertile soils annually all over the world (Nishanthiny *et al.*, 2010; Numaan 2011). Although, river water quality is threatened by point source pollution including municipal sewage discharges, industrial wastewater loads, diffuse contamination originating from intensive irrigated agriculture and nonpoint source pollution from agriculture (Saidi *et al.*, 2009). The water quality of any specific area or specific source can be assessed using physical, chemical and biological parameters. The values of these parameters are harmful to crop if they exceed certain threshold values.

However, river water quality varies from place to place and season to season. As rivers run through many communities, it could be fed with contaminants by runoff from different parts into the rivers. Unluckily, contaminated surface waters may not be profitable for agricultural purposes. Therefore, this study is to investigate the seasonal changes in quality indices and parameters of Ladokun river water and it is fitness for irrigation purposes.

MATERIALS AND METHODS

Study area

Ladokun River is located on the northern part of Ogbomoso land in Oyo state. It is along Ogbomoso – Ilorin old road. Ogbomoso is located on Latitude 8° 10’ N and Longitude 4° 10’ E, about 342 m above the mean sea level, southwest Nigeria. The study area has a bimodal rainfall pattern, with rainfall peaks in the months of June and September and break in August, with mean annual rainfall of approximately 1200 mm while the mean maximum temperature was not above 33°C and minimum temperature not below 16°C. The relative humidity of the area is not less than 80% between the months of April-November while it is low between December-March when dry wind (harmattan) blows from the northeastern part of the country Olaniyi (2006).

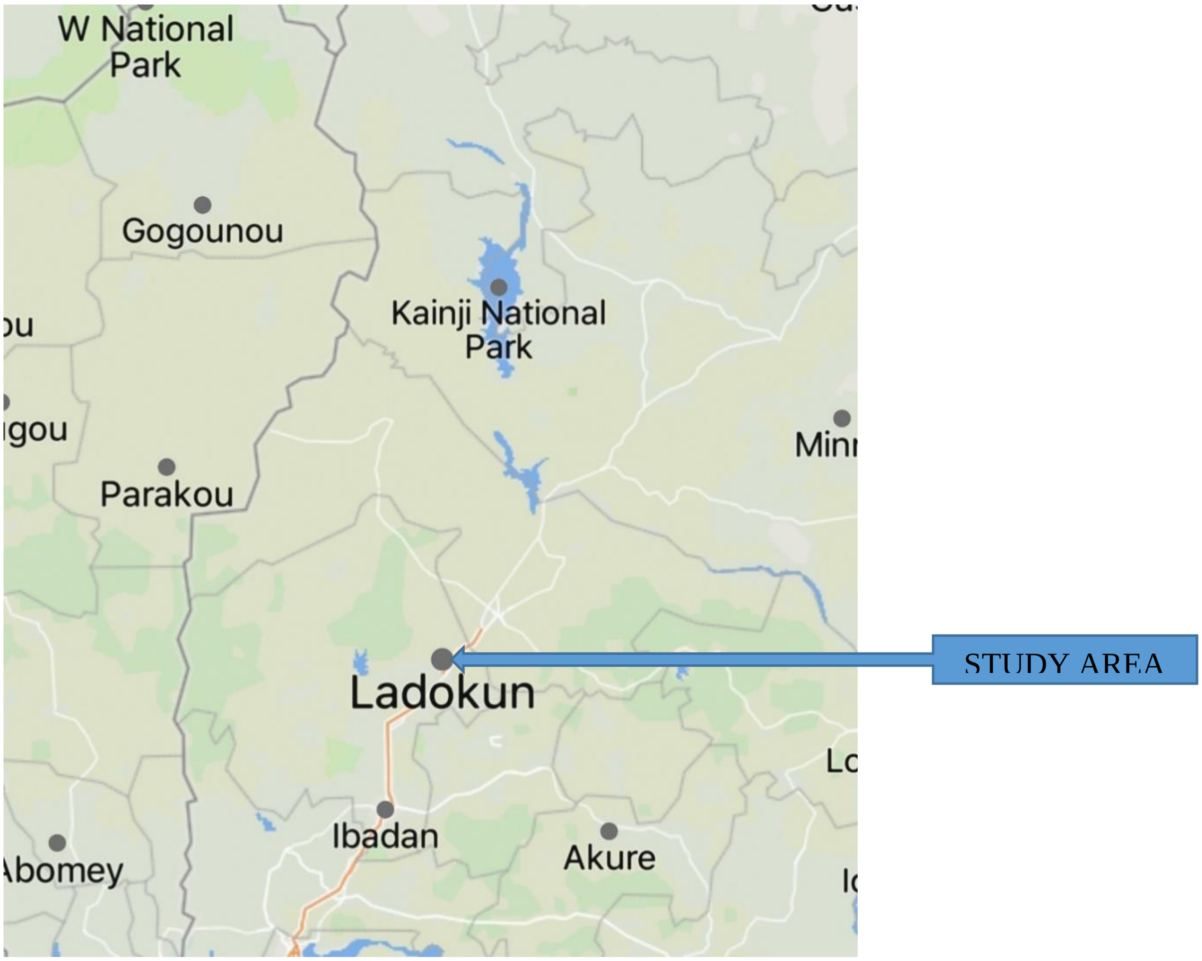

Figure 1: Map of Ladokun

Sample collection and analysis

The sampling date was chosen to correspond to the increase in the irrigation demand at the beginning of the dry season while the wet season was chosen during the mid-wet season. In this dry period irrigation becomes important at a period when water quality deteriorates in terms of salinity posing a major risk for irrigated soils and crops while the wet season was chosen when the water would have pushed away different discharges and waste along the river channel (Chabchoub 2011; CIHEAM, 1972).

For physiochemical properties purpose, sampling technique was applied to collect 18 samples of Ladokun river water into sterilized labelled bottles from different water points as early as 7:00 am for analyses. This research work conducted in November, 2018 for the dry season and July, 2019 for the wet season. After sampling, the bottles were marked, sealed and taken to the laboratory in ice-packed container for further analyses. The water quality indicators that were analyzed were: TDS, EC, Cl^-, pH, K^+, Na^+, Mg^{2+}, Ca^{2+}, PO_3-P, SO_4, NO_3-N, HCO^-_3 and CO_3 (All analyses were done according to APHA (2005) standard method. The concentrations of Na^+, Ca^{2+} and Mg^{2+} were used to quantify the sodium adsorption ratio (SAR) according to the equation:

$$\text{SAR} = \frac{Na^+}{\frac{\sqrt{Ca^{2+} + Mg^{2+}}}{2}} \qquad \ldots\ldots (1)$$

Where Na^+ is sodium concentration, meq/L; Ca^{2+} is calcium concentration, meq/L; Mg^{2+} is magnesium concentration, meq/L

Water samples analysis

Water sample analysis of Ladokun river in Ogbomoso were done for the major and minor ions (Mg^{2+}, Ca^{2+}, Na^+, and K^+) and anions (HCO_3, PO_4^{2-}, CO_3, SO_4^{2-} and NO_3) and other chemical parameters (SAR, SSP, RSC, PI, KR, MAR, TH and PS) was also evaluated by using standard empirical formulas. Beside this, measurements of EC, TDS, pH were done on the spot by means of a mercury thermometer and digital pH meter. The samples were then carefully sealed, labeled and taken for analysis. Chemical analyses were performed in the laboratory using Atomic Absorption Spectrophotometry for cations and conventional titration for anions Chopra and Kanwar (1980).

Data analysis

Data collected were subjected to descriptive statistics to determine the minimum, maximum, mean, standard deviation and coefficient of variation of the pooled data. Raw data and computed water quality indicators was subjected to analysis of variance (ANOVA) and means were separated by using Fisher`s least significant difference (LSD) test at 5% level of probability. SPSS (v. 20) and Grapher (version 10.0) software were used in the analyses. The analytical results were compared with the standard specification (Salifu *et. al*., 2017).

Residual sodium carbonate (RSC)

The residual sodium carbonate was calculated simply by subtracting the quantity of Ca^{2+} + Mg^{2+} from the sum total of carbonates and bicarbonates determined separately in a given sample and expressed in meq/L. Thus,

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+}) \ldots.. (2)$$

Sodium adsorption ratio (SAR)

Sodium adsorption ratio was calculated using the formula equation 3. The concentrations of Na^+,
Ca^{2+} and Mg^{2+} were used to determine the sodium adsorption ratio (SAR)

$$SAR = \frac{Na^+}{\frac{\sqrt{Ca^{2+} + Mg^{2+}}}{2}} \ldots\ldots (3)$$

Where, Na^+ is sodium concentration, meq/L; Ca^{2+} is calcium concentration, meq/L; Mg^{2+} is magnesium concentration, meq/L.

Soluble sodium percentage (SSP)

Wilcox (1955) has proposed classification scheme for rating irrigation water on the basis of soluble sodium percentage (SSP). The SSP was calculated by using following formula: $SSP = \frac{Na \times 100}{Ca+Mg+Na} \ldots\ldots (4)$

Where, the concentration of ions is expressed in meq/L.

Permeability index (PI)

The permeability index was calculated by the following formula:

$$PI = \frac{Na+\sqrt{HCO_3}}{Ca+Mg+Na} \times 100 \ldots\ldots (5)$$

Where, all the values are in meq/L.

Kelly's ratio (KR)

Kelly's ratio was calculated by using the following expression:

$$KR = \frac{Na+}{Ca^{2+}+Mg^{2+}} \ldots\ldots.. (6)$$

Where, concentrations are expressed in meq/L

Magnesium adsorption ratio (MAR)

Magnesium adsorption ratio was calculated by using the following expression:

$$MAR = \frac{Mg^{2+} \times 100}{Ca^{2+}+Mg^{2+}} \ldots\ldots (7)$$

Where, concentrations are expressed in (%)

Total hardness (TH)

Total hardness was calculated by using the following expression:

$$TH = \left\{ \left(2 \times \frac{Ca^{2+}}{40} \right) + \left(2 \times \frac{Mg^{2+}}{24} \right) \right\} \times 50 \quad \ldots\ldots (8)$$

Where, concentrations are expressed in mg/L

Potential salinity (PS)

$$PS = Cl^{-} + \frac{1}{2} SO_4^{2-} \quad \ldots.. (9)$$

Where, concentrations are expressed in meq/L

RESULTS

The analyzed physicochemical qualities of Ladokun river water were as indicated in table 1 and the descriptive statistics of the water quality indices for irrigation were as indicated in Table 2

Table 1: Descriptive statistics of the river water parameters for agricultural uses

Parameters		TDS	EC	Cl	pH	K+	Na^+	Mg^{2+}	Ca^{2+}	PO_3-P	SO_{42}	NO_3-N	HCO_3
Irrigation Standard		**2000**	**3.00**	**1065**	**6.0-8.5**	**2.00**	**400**	**61**	**400**	**2.00**	**960**	**10**	**620**
DRY SEASON	Min	25.00	0.05	6.50	6.89	1.90	1.28	5.00	10.00	0.06	21.00	0.03	120
	Max	25.00	0.05	9.24	7.16	2.10	1.92	6.00	12.00	0.08	25.00	0.04	120
	Mean	25.00	0.05	7.87	7.04	2.00	1.57	5.33	11.00	0.07	23.00	0.03	120
	Cv (%)	0.00	0.00	1.82	1.97	5.00	20.65	10.83	9.09	15.75	8.70	7.70	0.00
	SD	**0.00**	**0.00**	**0.17**	**0.14**	**0.10**	**0.32**	**0.58**	**1.00**	**0.01**	**2.00**	**0.00**	**0.00**
WET SEASON	Min	47.30	0.09	11.00	7.20	2.80	1.84	7.00	14.00	0.09	31.00	0.05	140
	Max	51.50	0.10	16.00	7.41	2.90	1.89	9.00	16.00	0.10	33.00	0.06	145
	Mean	49.40	0.10	13.50	7.30	2.83	1.86	8.00	15.33	0.10	32.00	0.06	141.7
	Cv (%)	4.45	0.00	8.53	1.44	2.04	1.35	12.50	7.53	5.97	3.13	7.78	2.04
SD		**2.23**	**0.00**	**0.57**	**0.11**	**0.06**	**0.03**	**1.00**	**1.15**	**0.01**	**1.00**	**0.00**	**2.89**

All parameters measured in mg L^{-1}, except EC (dS m^{-1}) and pH. (no unit); TDS: Total dissolved solid; EC: Electrical conductivity; TH: Total hardness; Min.: minimum; Max.: maximum; SD: standard deviation; CV: coefficient of variation; MPL: Maximum permissible limit; Irrigation standard: Salifu et al. (2017).

Table 2: Descriptive statistics of the water quality indices for irrigation

Parameters Indicator			TDS	EC	SSP	TH	RSC	SAR	PI	PS	KR	MAR
QUALITY	RATES	DRY SEASON	25.00	0.05	6.42	49.7	0.97	0.10	138.46	0.46	0.07	32.6
		WET SEASON	55.00	0.10	5.39	71.3	0.89	0.10	106.63	0.71	0.06	34.3

MAR: Magnesium absorption ratio, %, KR: Kelly's ratio, meq/L; PS: Potential salinity, meq/L; PI: Permeability Index, meq/L; SAR: sodium adsorption ratio, meq/L; RSC: Residual sodium carbonate, meq/L; TH: Total hardness, mg/L; SSP: Soluble sodium percentage, meq/L; EC: Electrical conductivity dS/m and Total dissolved solid

Source: Authors Fieldwork

Table 3: Summary of sampling point delineation under different limits (Meq/L)

Quality Class	Quality Standard
SAR	Sodium Adsorption Ratio
<10	Excellent
10 – 18	Good
18 – 26	Fair
>26	Unsuitable
PI	Permeability Index
<25	Unsuitable
25 – 75	Good
>75	Excellent
KR	Kelly's Ratio
< 1	Good
>1	Unsuitable
SSP	Soluble Sodium Percentage
< 50	Safe
> 50	Unsuitable
MAR (%)	Magnesium Adsorption Ratio
< 50	Acceptable
> 50	Non-acceptable
RSC	Residua Sodium Carbonate
< 1.25	Suitable
1.25- 2.50	Doubtful
>2.50	Unsuitable

Source: (Adhikary and Dash, 2012; Kerala,2014; Boateng *et al*., 2016

Table 4: Classification of irrigation water based on potential salinity (Meq/L)

Class of water/soil characteristics	**Class I**	**Class II**	**Class III**
Soil of low permeability	< 3	3-5	>5
Soil of medium permeability	< 5	5-10	>10
Soil of high permeability	< 7	7-15	>15

Source: Doneen (1961)

DISCUSSION

The observed pH values ranged from 6.89 to 7.16, with the mean values of 7.04 in dry season while pH values ranged from 7.20 to 7.41 with the mean value of 7.30 in wet season, both are tolerable to crops and within World Health Organization (WHO) limits. The water is good for agricultural use. The mean pH values indicated that the rivers did not have alkaline. Although, application of irrigation water with pH outside the threshold could cause nutritional disparity or lead to toxic ion build up in the soil (Ayers *et al*., 1985).

The potassium concentrations in the study water in dry season have a minimum, maximum and mean of 1.90mg/L, 2.10mg/L and 2.00 mg/L and 2.80mg/L, 2.90 mg/L and 2.83mg/ in wet season respectively; the maximum concentration in dry season and minimum, maximum and mean in wet season exceeds the threshold value of 2 mg/L. Inorganic fertilizers containing at least one of three basic nutrients; nitrogen, phosphorus, and potassium, are widely used in the study area to replenish crop and soil nutrients. Half to one-third of this fertilizer are absorbed by the crop and the remaining becomes residual in the soil and may join water body (Tomer and Burkart, 1998; Taiwo, 2016). Potassium is both an important fertilizer and common rocks constituent, high concentration of potassium ion found in the water could have been induced by leachates from agricultural fertilizer as observed by Falowo *et* al., (2017) or dissolution of rock constituent. A major concern of high potassium concentrations in irrigation water is its deleterious effects on soil hydraulic properties, which has negative impacts on infiltration, water availability and plant growth (Oster *et al.,* 2016).

Sodium (Na^+) content is another major indicator when evaluating irrigation water quality. The detection of sodium toxicity is relatively difficult compared to the toxicity of other ions. Typical toxicity symptoms on the plant are leaf burn, scorch and dead tissue along the outside edges of leafs. However, its concentrations ranged from 1.28mg/L to 1.92 mg/L with a mean value of 1.57mg /L during the dry season and was 1.84 mg/L to 1.89mg/L with a mean value of 1.86mg/L in wet season; The ranged and mean values were less than 400mg/L (Salifu *et al.,* 2017), indicating no restriction of use. Irrigation water with high sodium (Na^+) content could cause the displacement of exchangeable cations, such as Ca^{2+} and Mg^{2+}, from the soil clay minerals, which would be replaced by Na^+ (Matthess *et al.,*1982) stated that soils saturated by sodium peptize and they lose their permeability, leading to decrease in fertility and their suitability for cultivation.

High concentrations of Ca^{2+} and Mg^{2+} ions in irrigation water will cause increase in soil pH, leading to reduction in the availability of phosphorous to plants (Al-Shammri *et al*., 2005). According to Khodapanah *et al.,* (2009), water containing Ca^{2+} and Mg^{2+} above 400mg/L and 61 mg/L respectively, are not suitable for irrigation. The observed concentrations of these elements was not more than 12mg/L and 6 mg/L for Ca^{2+} and Mg^{2+} in dry season, 16mg/L and 9mg/L in wet season respectively, this indicated that none of the samples exceeded the threshold value.

Phosphate (PO_3-P) in irrigation water are more of fertility issue, however high levels of PO_3-P in the water sources is not desirable, as it is an indication of eutrophication of surface water bodies (Davis *et al.* 2001). Although, the total phosphate concentration of the Ladokun River during dry season ranged from 0.06mg/L to 0.08 mg/L with a mean value of 0.07 mg /L; and in wet season ranged from 0.09mg/L to 0.10 mg/L with a mean value of 0.10mg /L; (Table 1). When excess nitrogen and phosphorus are transported to surface water, they cause eutrophication and elevated algal (Davis *et al.,* 2001). Waters with elevated N can also cause quality problems in crops such as barley and sugar beets as well as excessive vegetative growth in vegetables, thus delaying fruit setting and maturity (Bauder *et al.,* 2014).

Sulphates (SO_4^{2-}) are naturally occurring in surface waters. However, discharges from industries as well as atmospheric precipitation could add significant quantities to surface waters (Khudair, 2013). The concentrations of SO_4^{2-} in the studied water ranged from 21mg/L to 25 mg/L with a mean value of 23.00 mg/L in dry season and ranged from 31mg/L to 33mg/L with a mean value of 32 mg/L in wet season (Table 1). These values were within the maximum limit of 960 mg/L (Salifu *et al*., 2017), however, indicating no threat.

The mean and maximum Nitrate nitrogen (NO_3-N) concentration in the studied water is 0.03mg/L and 0.04mg/L, for dry season while 0.06mg/L and 0.06mg/L, in wet season respectively. This values fall below the maximum limit of 10mg/L recommended for irrigation purposed by (FAO, 1989). The low level of NO_3-N concentration in the water could be attributed to a low percentage of cropland within the study area that indicates lower nitrogen based fertilizer were used. This lends credence and confirms the assertion of (Wick *et al*., 2012) and (Keeney *et al.,* 2014) who observed a similar trend. Nitrogen is a major nutrient needed by the plant, its abundance is desired in irrigation water; though low concentration of it (as in the water studied) does not make the water unfit for irrigation.

Bicarbonate brings about a change in soluble sodium percentage, hence regulate sodium hazard. Bicarbonate in the studied River water ranged within 120mg/L having mean values of 120mg/L, in dry season while in the wet season ranged from 140mg/L to 145mg/L, having mean values of 141.7mg/L and the maximum bicarbonate permissible limit is 620mg/L (FAO, 1989), therefore, the values are within permissible limit. It has no traced of carbonate due to the pH of the water.

Fitness of Ladokun river water for agricultural uses

Too much of salts of calcium, magnesium, sodium and potassium present in the irrigation water maybe delicate and injurious to the plants. However, they reduced the osmotic activities of the plants and may avert sufficient aeration. The salt concentration in water of Ladokun river in Ogbomoso ranged within 25.00mg/L with a mean of 25.00mg/L for dry season and ranged from 47.30mg/L to 51.50mg/L with a mean of 49.40mg/L in wet season (Table 1); the higher concentration is below the permissible limit of the standards 2000mg/L (FAO, 1985), also according to irrigation water quality classification by (Ayers *et al*., 1985), the values fall within permissible limit for irrigation (< 450mg/l) and they had no restriction. The value of the coefficient of variation was 0.00mg/l, indicated that the TDS of water in the study area varied. Electrical conductivity in this study for irrigation water quality, it values ranged within 0.05dS/m with a mean of 0.05dS/m in dry season and 0.09dS/m to 0.10dS/m with a mean of 0.10dS/m in wet season (Table 1); The sample falls within the standard irrigation water categories as the maximum limit for irrigation water was prescribed as 3dS/m (Table 1), thus, the water is suitable for irrigation use in terms of EC and TDS.

Wilcox (1955) has proposed classification scheme for rating irrigation waters on the basis of soluble sodium percentage (SSP). The values of SSP less than 50meq/L indicate good quality of water and higher values (i.e. > 50meq/L) shows that the water is unsafe for irrigation (USDA, 1954). From these figures, it is observed that, 100 per cent of the water in dry season as well as wet season has good quality water and safe for irrigation purposes. Total hardness simply means the sum of calcium and magnesium. The values of total hardness varied from 49.7 to 71.3mg/L with an average of 60.5mg/L where the maximum value is below the prescribed limit for irrigation water of 712 mg/L set by (FAO, 1989). The low values of total hardness are probably due to the presence of alkaline earth ions (Ca^{2+} and Mg^{2+}) of weak acids (HCO_3^- and CO_3^-) and strong acids (Cl-, SO_4^{2-} and NO_3) (Roy *et. al.*, 2018; Rao et. *al.*, 2012). Therefore, low alkalinity values reflect immature hydrochemistry of surface water during seepage and hypodermic flow (Demetriades, 2011). The water sample was classified as hard water during dry season and very hard in wet season.

The Residual Sodium Carbonate (RSC) did not exceed value of 2.5meq/L in dry and wet season; the water is generally suitable for irrigation. If the value of RSC is between 1.25meq/L and 2.5meq/L, the water is doubtful (Table 4) while a value less than 1.25meq/L indicates safe water quality (Cuena, 1989). In this respect, it is evident from (Table 3), that, RSC values in dry season as well as rainy season are less than 1.25meq/L indicates safe water quality, suggesting that, the study location is under safe limit for irrigation use.

The waters having SAR values less than 10meq/L are considered excellent, 10meq/L to 18meq/L as good, 18meq/L to 26meq/L as fair, and above 26meq/L are unsuitable for irrigation use USDA (1954). In this research work, the SAR values are lesser than 10meq/l for the samples taken in dry and wet season, therefore it is graded as excellent for irrigation use (Table 3). SAR is a measure of tendency of sodium (Na) ion to displace Ca^{2+} ion in the irrigation water soil Al-Tabbal and AlZboon (2012).

The Permeability Index (PI) values > 75meq/L indicates excellent quality water for irrigation. If the PI values are between 25meq/L and 75meq/L, it indicates good quality of water for irrigation. However, if the PI values are less than 25meq/L, it shows unsuitable nature of water for irrigation (Table 3). Permeability Index (PI) of water is a function of sodium, calcium, Magnesium and carbonate in the soil (Vasanthaiviger, 2010; Stewart and Hielsen, 1990). Based on this assessment, the water samples from this location indicate excellent quality of water in dry season as well as wet season, therefore suitable for irrigation purposes.

Potential salinity (PS) is an important parameter for assessing the suitability of water for irrigation uses, the water samples from the study river ranged from 0.46meq/L to 0.71meq/L from dry to rainy season with an average of 0.59 meq/L. This indicated that the water samples from the study area is good for irrigation purposes in both dry and wet season and on soil of low permeability and on class I (Table 4). PS means chloride concentration plus half of the sulfate concentration (Doneen, 1961).

area has good quality water for irrigation purposes due to non-alkali hazards in the water.

Magnesium content of water is very important criteria in determining irrigation water quality. In most of the water, calcium and magnesium maintain a state of equilibrium. Too much content of magnesium in water use for irrigation will negatively affect crop yields as the salinity of the soils increases (Joshi *et al.,* 2009). The values of the magnesium adsorption rate of the water sampled in this study varies from 32.6 to 34.3 % (Table2) from dry to wet season, showing that it is below the maximum limit of 50% (Table 3)

The Kelly's ratio of unity or less than one is indicative of good quality of water for irrigation whereas above one is suggestive of unsuitability for agricultural purpose due to alkali hazards (Karanth, 1987). Kelly's ratio values of greater and less than unity describes the sampled water as being not suitable and suitable for irrigation respectively (Table 4) (Sundaray *et al*., 2009). From these figures, both in dry season as well as wet season were observed to be 100 per cent good. The

Ayers and Westcot (1985). The water is therefore considered acceptable and suitable for irrigation. However, high magnesium adsorption ratio usually has negative effect to soil when it exceeds 50%.

CONCLUSIONS

Based on this study, Ladokun River in Ogbomoso was examined for its fitness for irrigation use. It is found suitable for irrigation purposes, and appropriate management measures are suggested to safeguard the quality of this resource and could be used on almost all soils.

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