

# Seasonal Assessment of the Physico-Chemical Properties of Groundwater in Some Villages Around an Iron and Steel Recycling Industry in Southwestern Nigeria

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**Abstract** This study assessed the physico-chemical quality parameters of ground water bodies around the industry, with a view to evaluating the impact of the water bodies for the industry, and by extension the health of people of neighbouring communities who depend on these groundwater bodies for their water needs for domestic and other purposes. Water samples were collected from five ground water bodies. Physico-chemical analysis was carried out on the samples using standard methods. The highest and least values of turbidity ( $44.47 \pm 34.37$  and  $7.99 \pm 1.89$  NTU) were recorded in the well and borehole during the wet season respectively. Highest value of pH ( $6.65 \pm 0.13$ ) was recorded in the well during the dry season, while the least value ( $5.94 \pm 0.15$ ) was found in borehole water sample during the wet season. TDS was highest ( $113.23 \pm 14.76$  mg/L) in the well during the dry season, while it was least ( $71.69 \pm 17.68$  mg/L) in the borehole during the wet season. Least value of DO ( $4.20 \pm 0.71$  mg/L) and the highest value ( $6.00 \pm 0.42$  mg/L) were recorded during the dry season, in borehole and well respectively.  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  were highest in the well during the wet season ( $26.31 \pm 5.64$  and  $16.08 \pm 2.28$ ) mg/L respectively but their least values  $16.37 \pm 3.67$  and  $8.91 \pm 1.46$  respectively occurred in the borehole during the dry season. Highest values of Cd ( $0.093 \pm 0.0043$  mg/L), Fe ( $0.69 \pm 0.05$  mg/L) and Pb ( $0.24 \pm 0.03$  mg/L) were recorded in the borehole during the dry season, but the least value of Cd ( $0.086 \pm 0.0028$  mg/L) was found in the well during the dry season, while least values for Fe and Pb ( $0.27 \pm 0.036$  and  $0.012 \pm 0.0086$ ) mg/L respectively were found in the well during the wet season. The study concluded that values of turbidity, dissolved oxygen, cadmium, lead and iron significantly exceeded the national (NSDWQ) and international (WHO) permissible limits. The high values of these parameters, especially turbidity and heavy metals, may make the water toxic, and pose serious health challenges to people who drink the water.

**Keywords:** groundwater bodies, industry, iron, physico-chemical, seasonal, health, permissible limits

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## 1. Introduction

Ground water, which because it is out of sight, it is frequently out of mind [1], represents 30.1% of the world's freshwater distribution [2]. The ground water regime is a dynamic system in which water is continuously in motion through the recharge (water entering) and discharge (water leaving) system, which can be naturally occurring or influenced by human activity. Ground water is a major source of water that is readily available for human use, such as domestic (potable and non-potable), agricultural and industrial. These human activities put pressure on ground water, thereby leading to a reduction in the remaining portion available, as well as lowering of the quality of the ground water [3,4,5]. Ground water quality comprises the physical, chemical and biological qualities [6]. It becomes

contaminated when either the physico-chemical or the biological property is disturbed. The inability of government to meet the rising water need of the people has made them to look for alternative ground water sources such as shallow wells and boreholes [7,8].

Ground water pollution usually results from human activity, when pollutants are released to the ground, and they make their way down into ground water. Natural sources of pollution of ground water include contamination by minor and unwanted constituents, or other source of impurity [6]. Major threats to ground water quality are from diffuse sources of contamination. These sources of contamination include introduction into the air and subsequently rained out, agricultural use and partly infiltrate into the subsurface, mine tailings and accidental spills of hazardous substances, as well as wastewater from industrial processes. Understanding the physical environment of groundwater is important in the assessment of its

quality's parameters, and pollution evaluation. There is high risk of vulnerability to contamination in areas where population density is high, and there is intensive land use. When ground water becomes contaminated, it is difficult and expensive to clean up. In Nigeria, especially in urban and semi-urban areas, increased urbanization, industrialization and agricultural activities pose serious pollution threats, with all its attendant health hazards, to ground water quality [9,10]. Ground water may contain fluoride, and toxic metals such as arsenic, lead and selenium in quantities that are harmful to health, as well as iron and manganese which cause other types of problems such as the staining of sanitary fixtures. The inability of government to meet the rising water need of the people has made them to look for alternative ground water sources such as shallow wells and boreholes [7,8]. Sustainable ground water management must be based on prevention of over exploitation of ground water resources, and on the prevention of contamination [11].

Scrap metals are among the most important priced materials in Municipal Solid Waste [12]. Many important metals including iron and steel, copper, brass, and aluminum have been recovered and recycled [13,14]. "Reference [15] also reported that in the USA, recycling metals contributed 76.9 metric tons of metal valued at \$14.2 billion or 58% of apparent metal supply". The recycling of scrap steel obtained mostly from municipal solid wastes is now a major way through which the Nigeria steel sector is being sustained. "Reference [12] reported that in many of the rolling mills, 100% scrap steel is recycled for the production of iron bars used for civil construction". Scrap metal recycling results in the generation of less than 7% and 7 - 15% slag for low and high carbon steel respectively [12]. In Nigeria, metal scrap is useful both as source of raw material, and as a solid waste management method. Hence, recycling of scrap is advantageous in converting materials that would have otherwise constituted various forms of environmental hazards into useful forms [16,17]. However, lack of required strict regulations for environmental and personnel protection, as well as poor investment in facilities necessary for improving their production processes have hampered the acceptability and hence, rapid growth witnessed by the scrap metal recycling industry in Nigeria.

The principal sources of pollution caused by smelting are contaminant-laden air emissions and process waste such as wastewater and slag [18]. One type of pollution attributed to air emissions is acid rain [18]. During smelting, sulfide ores emits sulphur (IV) oxide, which reacts chemically with water vapour, oxygen and other gases in the atmosphere to form a sulphuric acid mist, and then falls back to the earth surface in form of acid rain, or other forms of wet deposition. As this acid rain falls to the earth, it increases the acidity of soils, streams, and lakes, harming the health of vegetation, fish and wildlife populations, and ultimately humans [18]. Percolation of the acidic rain water into the soil may dissolve harmful elements and indirectly affect groundwater distribution systems [19].

Also, complex geochemical processes in soils are important factors in determining the quality of the percolate which infiltrates down to ground water systems [20].

The Ife Metal Recycling Industry which was established in January 2011, uses electric arc furnace to produce iron bar from the scrap collected from various dumping area across the country. The industry has a potential for causing strong environmental pollution, due to emissions which can degrade the soil, vegetation and water, and also increase the rate of occurrence of some common diseases in residents of some rural communities in its immediate vicinity. The inhabitants of these villages depend on untreated ground water bodies like hand-dug wells and "boreholes" for their daily water needs.

However, there is paucity of information on the physicochemical properties of ground water bodies in the vicinity of the Metal Recycling Industry in the Southwestern part of Nigeria in which this study is based. There is therefore the need to assess the impact of the activities of the industry on the physicochemical properties of the ground water bodies in these communities, hence this study.

## 2. Materials and Methods

### 2.1. Study Area

The Ife Metal Recycling Industry is located in Fasina Area, Ile-Ife, Ife Central Local Government, Osun State. The coordinates of the Industry lies on latitude 7°29'44"N and longitude 4°28'37"E. The study was carried out in 4 villages (Awosun, Coker, Fasina and Ogunwusi) located around the Ife Iron and Steel Recycling Industry (Figure 1). The land-use consists of a mosaic, principally of degraded tropical forest, arable land and built-up areas. The climate is tropical with the raining season extending from April to October while the dry season lasts from October to March [21]. However, due to human activities such as industrialization, urbanization and agriculture, the region has been witnessing rapid population growth and land-use conversion.

### 2.2. Sampling Stations

The study was carried out on the five ground water bodies in four villages around the industry. A Global positioning system (GPS) handset was used to determine the grid coordinates of the sampling stations (Table 1). The five sampling stations were: two hand-dug wells in Awosun Village and one borehole each in Fasina, Coker and Ogunwusi villages. Five water samples were collected from the five sampling stations. Sampling was carried out six times for a period of ten months, covering both the dry and wet seasons. At each sampling station, water samples were collected using clean, properly washed and rinsed 2-litre plastic bottle containers. All possible sources of contamination were taken into consideration while performing the analysis.

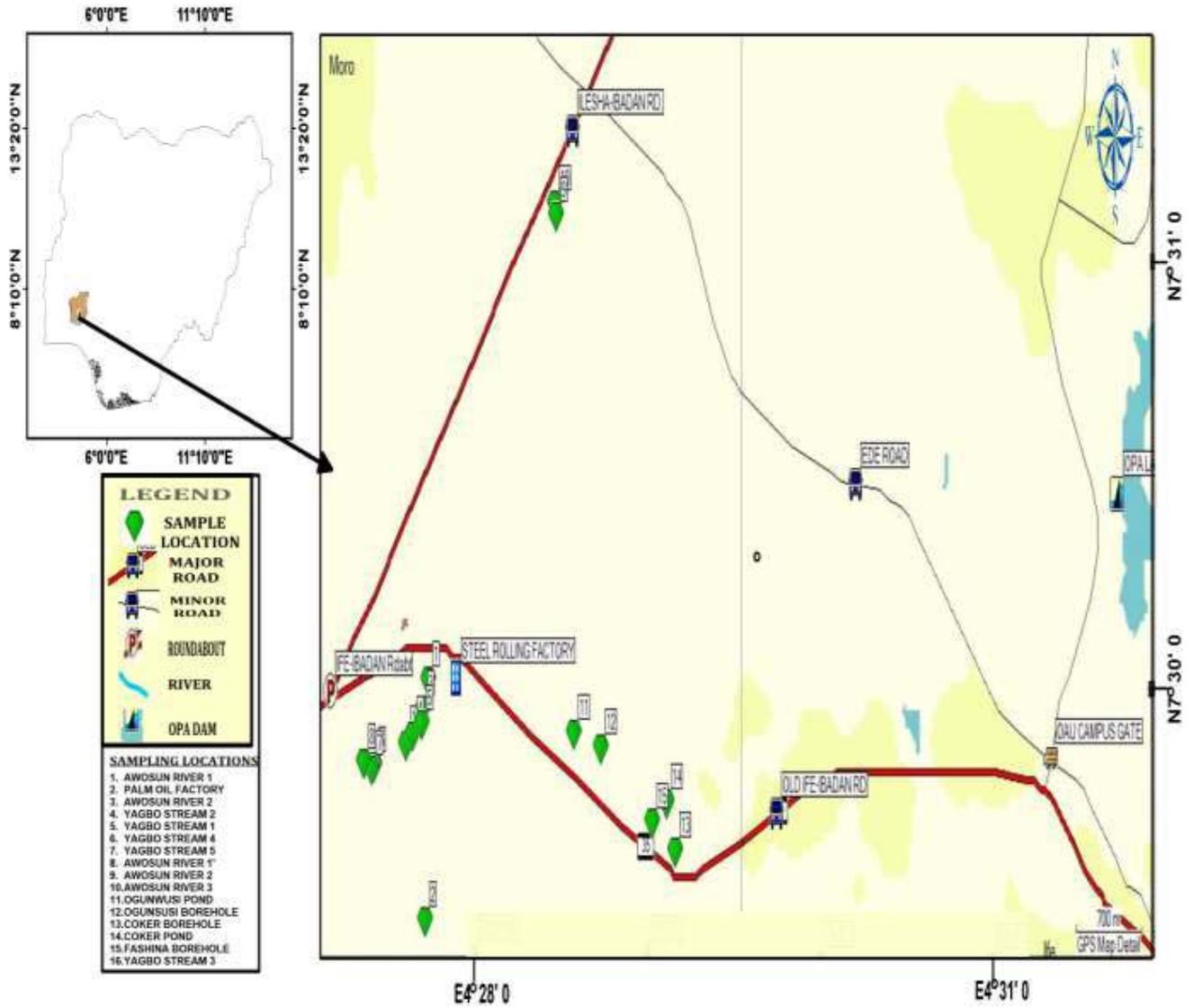


Figure 1. Map of study area showing sampling points

Table 1. THE GEOGRAPHICAL LOCATIONS OF WATER SAMPLING STATIONS

S/N	Sampling Stations	Grid Co-ordinates		Elevation (m)Amsl
		Northing	Easting	
1	Awosun Well 1	07° 30' 01.0"	004° 27' 43.8"	240
2	Awosun Well 2	07° 29' 56.9"	004° 27' 42.1"	238
3	Coker Borehole	07° 29' 37.1"	004° 29' 09.3"	247
4	Fasina Borehole	07° 29' 41.3"	004° 29' 01.6"	241
5	Ogunwusi Borehole	07° 29' 51.7"	004° 28' 43.7"	248

Amsl: Above Mean Sea Level.

### 2.3. Physicochemical Analysis of the Water Samples

Water and ambient air temperature were determined using a thermometer, while pH was measured in situ, using a pH meter. The electrical conductivity and Total Dissolved Solids (TDS) were determined in situ using a Jenway Conductivity meter. Titrimetric methods described by [14] were used to determine ions of magnesium and calcium, dissolved oxygen (DO) and biochemical oxygen demand (BOD<sub>5</sub>). Turbidity was determined using nephelometric method as outlined by [22]. Potassium ion and sodium ion were analyzed using flame emission

spectrophotometer as specified by [23]. Nitrate was determined spectrophotometrically as described [24]. Heavy metals were determined using atomic absorption spectrophotometer [23].

### 2.4. Quality Control and Quality Assurance

All determinations were based on standard scientific methods with relevant quality assurance and quality control (QA/QC) measures. Some of the measures adopted include the use of non - phosphate detergents to wash the DO and BOD bottles after which it was rinsed with distilled water before use since phosphate can stimulate

algal growth. The bottles were then thoroughly rinsed with the water sample before collection of the water samples for analyses. Labelling of the bottles was done on the field using a marker to prevent sample mix up. The equipment used to determine the physicochemical water quality parameters were standardized using the blanks and standards of known concentrations before each determination [24]. All the determination of physico-chemical water quality parameters were carried out within the individual holding time for the samples [24] and replicate determinations were carried out.

### 3. Results and Discussions

All the five groundwater stations available within the study area (Table 1) were sampled and analysed. The least mean values of water temperature ( $26.22 \pm 0.41^\circ\text{C}$ ) and turbidity ( $7.99 \pm 1.89$  NTU) were recorded in the borehole during the wet season as presented in Table 2 while the highest mean values of water temperature ( $28.00 \pm 0.26^\circ\text{C}$ ) and turbidity ( $44.47 \pm 34.37$  NTU) occurred in the well during the wet season. There was a very high significant difference ( $P < 0.001$ ) in water temperature values in the water bodies, while turbidity showed a high significant difference ( $P < 0.01$ ) across the water bodies (Table 2). The higher value of turbidity recorded in the wet season could be attributed to input of silt, and an increase in abundance of phytoplankton biomass (which influences water transparency, and therefore turbidity) and organic matter with run-off. Higher turbidity obtained in this study than the national standard was indicative of pollution of the water bodies, and may lead to negative health impact on the residents of the study area. According to [25], high turbidity is often associated with higher level of disease-causing microorganisms, such as bacteria and parasites. Also, [26] reported that turbid water has the tendency of posing health challenges, causing symptoms like nausea, cramps, diarrhea and associated headaches. The highest mean value of  $191.3 \pm 104.46$  mg/L for total suspended solids (TSS), occurred in the well during the wet season, while the least mean value of  $93.64 \pm 10.49$  mg/L was found in the borehole during the dry season (Table 2). A significant difference ( $P < 0.05$ ) existed in

TSS across the water bodies (Table 2). Higher TSS found in wet season could be as a result of rainfall which is usually coupled with increase in organic sources (algae, protozoa and decay of vegetation such as humic substances, tannins and lignins). Equally, higher turbidity and TSS values found in the well in wet season in this study might have been aided by the shallowness of the wells in comparison with the boreholes which makes them to be easily impacted by pollutants. This is supported by [27] who stated that shallow wells are susceptible to contamination from activities around.

The highest mean values of pH ( $6.65 \pm 0.13$ ), conductivity ( $172.12 \pm 11.33 \mu\text{Scm}^{-1}$ ) and TDS ( $113.23 \pm 14.76$  mg/L) were from the well water samples during the dry season, while the least values of conductivity ( $117.22 \pm 28.10 \mu\text{Scm}^{-1}$ ) and TDS ( $71.69 \pm 17.68$  mg/L) were found in the borehole samples in the wet season (Table 3). There was a significant difference in the values conductivity and TDS across the water bodies at  $P < 0.05$ . On the other hand, the least value of pH ( $5.94 \pm 0.15$ ) occurred in the well water samples during the wet season. There was a high significant difference ( $P < 0.01$ ) in the values of pH across the water bodies. From the above results, the pH of water samples were within the permissible range of 6.5-8.5 national standard given by Nigerian Standard for Drinking Water Quality [28]. The slight acidic pH recorded in this study agrees with [29] and [30] who studied soil, and surface water and sediment around the vicinity of the same scrap metal recycling industry respectively. The sulphur (iv) oxide that is formed from the byproduct of the activities of the metal smelting industry could contribute to the pH of the water body that is in the acidic range and falling below permissible range. Acidic pH range of the groundwater water samples is of concern since pH affects the solubility of metals in solution, and indirectly impacts physiological process in a great way [28,31]. TDS value was below the recommended national standard. References [32,33] rated TDS levels as follows: excellent =  $< 300$  mg/L; good =  $300-600$  mg/L; fair =  $600-900$  mg/L; poor =  $900-1200$  mg/L; unacceptable =  $> 1200$  mg/L. Reference [34] and [32] reported that TDS may affect the taste of water, and drinking water with extremely low TDS concentration may be unacceptable because of its flat insipid taste, thereby affecting the palatability.

Table 2. SEASONAL VARIATION IN PHYSICAL PARAMETERS OF WATER SAMPLES FROM THE WATER BODIES

Parameter	Borehole		Well		Overall mean		F	P	NSDWQ	WHO
	Wet	Dry	Wet	Dry	Wet	Dry				
Air Temp ( $^\circ\text{C}$ )	$26.83 \pm 0.56^{ab}$	$28.03 \pm 1.25^b$	$26.33 \pm 1.03^{ab}$	$25.67 \pm 1.23^a$	$27.30 \pm 0.54$	$29.09 \pm 0.90$	1.804	.095	NG	NG
Water Temp ( $^\circ\text{C}$ )	$26.22 \pm 0.41^{cdef}$	$27.33 \pm 0.42^f$	$28.00 \pm 0.26^{ef}$	$27.57 \pm 0.19^{def}$	$26.63 \pm 0.38$	$28.13 \pm 0.38$	8.813	.000***	NG	NG
Turbidity (NTU)	$7.99 \pm 1.89^a$	$14.52 \pm 5.14^a$	$44.47 \pm 34.37^a$	$33.04 \pm 24.21^a$	$12.56 \pm 4.72$	$13.65 \pm 3.56$	2.915	.009**	5	NG
TSS (mg/L)	$106.09 \pm 19.33^a$	$93.64 \pm 10.49^a$	$191.3 \pm 104.46^a$	$136.77 \pm 38.51^a$	$102.75 \pm 13.15$	$97.49 \pm 11.04$	2.552	.019*	500	NG
App Color (Pt-Co)	$118.61 \pm 24.43^a$	$246.56 \pm 42.98^a$	$417.16 \pm 285.82^a$	$502.45 \pm 219.86^a$	$105.82 \pm 17.23^a$	$233.76 \pm 29.36$	3.583	.002**	NG	NG
True Color (Pt-Co)	$40.42 \pm 8.34^a$	$47.53 \pm 14.55^a$	$65.30 \pm 41.84^a$	$65.30 \pm 26.97^a$	$37.58 \pm 6.40$	$52.50 \pm 11.02$	4.253	.001**	NG	NG

$P < 0.05$  = \* Significant difference;  $P < 0.01$  = \*\* Highly significant difference;  $P < 0.001$  = \*\*\* Very highly significant difference; Mean values with the same alphabets as superscripts along the rows are not statistically significantly different; NG = No Guideline; NSDWQ, 2007 = Nigeria Standard for Water Quality.

Table 3. SEASONAL VARIATION IN CHEMICAL PARAMETERS OF WATER SAMPLES IN THE WATER BODIES

Parameters	Borehole		Well		Overall mean		F	P	NSDWQ	WHO
	Wet	Dry	Wet	Dry	Wet	Dry				
pH	6.49 ± 0.87 <sup>ab</sup>	6.28 ± 0.21 <sup>ab</sup>	5.94 ± 0.15 <sup>a</sup>	6.65 ± 0.13 <sup>bcd</sup>	6.35 ± 0.08	6.15 ± 0.18	3.686	.002**	6.5 - 8.5	NG
Acidity (mg/L)	9.56 ± 0.88 <sup>a</sup>	9.22 ± 2.08 <sup>a</sup>	7.50 ± 0.43 <sup>a</sup>	13.83 ± 5.31 <sup>a</sup>	9.00 ± 0.68	9.80 ± 1.84	.733	.667	NG	NG
Alkalinity (mg/L)	50.89 ± 8.17 <sup>abc</sup>	55.78 ± 8.61 <sup>ab</sup>	30.33 ± 6.84 <sup>a</sup>	36.67 ± 4.86 <sup>a</sup>	47.47 ± 5.50	46.67 ± 5.97	3.192	.005**	NG	NG
Conductivity (µS <sup>cm</sup> <sup>-1</sup> )	117.22 ± 28.10 <sup>ab</sup>	158.7 ± 16.90 <sup>b</sup>	125.58 ± 23.42 <sup>ab</sup>	172.12 ± 11.33 <sup>ab</sup>	126.79 ± 21.90	182.34 ± 18.86	2.582	.018*	1000	250
TDS (mg/L)	71.69 ± 17.68 <sup>abc</sup>	95.24 ± 10.20 <sup>c</sup>	75.35 ± 14.07 <sup>abc</sup>	113.23 ± 14.76 <sup>bc</sup>	77.25 ± 13.57	109.17 ± 11.20	2.520	.020*	500	NG
Hardness (mg/L)	37.65 ± 7.24 <sup>ab</sup>	31.26 ± 4.47 <sup>ab</sup>	52.50 ± 10.13 <sup>b</sup>	37.64 ± 4.85 <sup>ab</sup>	36.01 ± 4.45	31.32 ± 3.57	1.766	.102	NG	NG
DO (mg/L)	5.24 ± 0.48 <sup>a</sup>	4.20 ± 0.71 <sup>ab</sup>	5.13 ± 0.19 <sup>ab</sup>	6.00 ± 0.42 <sup>ab</sup>	4.91 ± 0.35	4.76 ± 0.53	1.639	.134	5.0	NG
BOD (mg/L)	2.13 ± 0.23 <sup>a</sup>	2.18 ± 0.37 <sup>a</sup>	1.93 ± 0.55 <sup>a</sup>	3.10 ± 0.41 <sup>a</sup>	2.35 ± 0.21	2.47 ± 0.36	.763	.650	6.0	NG
NH <sub>3</sub> (mg/L)	0.18 ± 0.01 <sup>ab</sup>	0.19 ± 0.01 <sup>ab</sup>	0.17 ± 0.02 <sup>ab</sup>	0.13 ± 0.01 <sup>a</sup>	0.18 ± 0.02	0.17 ± 0.02	1.782	.099	NG	NG
OM (mg/L)	5.34 ± 0.97 <sup>abc</sup>	2.52 ± 0.58 <sup>a</sup>	3.02 ± 0.45 <sup>ab</sup>	4.17 ± 1.64 <sup>abc</sup>	5.17 ± 0.68	2.06 ± 0.30	2.690	.014*	NG	NG
TOC (mg/L)	3.11 ± 0.56 <sup>abc</sup>	1.46 ± 0.34 <sup>a</sup>	1.75 ± 0.26 <sup>ab</sup>	2.43 ± 0.95 <sup>abc</sup>	3.01 ± 0.40	1.20 ± 0.23	2.691	.014*	5	NG
Ca <sup>2+</sup> (mg/L)	22.46 ± 5.35 <sup>ab</sup>	16.37 ± 3.64 <sup>ab</sup>	26.31 ± 5.64 <sup>b</sup>	16.88 ± 3.20 <sup>ab</sup>	19.85 ± 3.32	15.16 ± 2.55	1.804	.095	NG	75
Mg <sup>2+</sup> (mg/L)	1.32 ± 0.37 <sup>a</sup>	1.84 ± 0.30 <sup>a</sup>	1.34 ± 0.17 <sup>a</sup>	1.83 ± 0.37 <sup>a</sup>	1.30 ± 0.03	1.85 ± 0.26	1.011	.446	0.20	50
Na <sup>+</sup> (mg/L)	10.01 ± 0.84 <sup>a</sup>	9.16 ± 2.65 <sup>a</sup>	11.30 ± 2.11 <sup>a</sup>	6.18 ± 2.50 <sup>a</sup>	12.95 ± 1.40	13.31 ± 2.76	1.647	.132	200	200
K <sup>+</sup> (mg/L)	5.74 ± 1.26 <sup>a</sup>	6.70 ± 1.81 <sup>a</sup>	8.85 ± 1.93 <sup>a</sup>	7.59 ± 0.90 <sup>a</sup>	7.78 ± 1.45	9.10 ± 1.52	1.377	.228	NG	NG
Cl <sup>-</sup> (mg/L)	8.91 ± 1.46 <sup>b</sup>	9.88 ± 1.09 <sup>b</sup>	16.08 ± 2.28 <sup>ab</sup>	14.63 ± 3.80 <sup>ab</sup>	12.59 ± 2.49	14.39 ± 2.55	2.402	.026*	250	250
SO <sub>4</sub> <sup>2-</sup> (mg/L)	7.71 ± 1.65 <sup>ab</sup>	13.77 ± 1.89 <sup>ab</sup>	14.44 ± 2.92 <sup>ab</sup>	13.22 ± 2.05 <sup>ab</sup>	8.85 ± 1.12	13.77 ± 1.25	1.390	.222	100	500
NO <sub>3</sub> <sup>-</sup> (mg/L)	4.13 ± 0.40 <sup>abc</sup>	4.19 ± 0.27 <sup>c</sup>	4.97 ± 0.52 <sup>bc</sup>	5.80 ± 0.37 <sup>c</sup>	4.24 ± 0.35	4.98 ± 0.36	3.546	.002**	50	50
HCO <sub>3</sub> <sup>-</sup> (mg/L)	61.07 ± 9.80 <sup>a</sup>	66.93 ± 10.33 <sup>a</sup>	36.40 ± 8.21 <sup>a</sup>	44.00 ± 5.84 <sup>a</sup>	56.96 ± 6.60	56.00 ± 7.17	4.253	.001**	NG	NG

0.05=\* Significant difference; P<0.01=\*\* Highly significant difference; P<0.001=\*\*\* Very highly significant difference; Mean values with the same alphabets as superscripts along the rows are not statistically significantly different; NG = No Guideline; NSDWQ, 2007 = Nigeria Standard for Water Quality.

Dissolved oxygen (DO) and biochemical oxygen demand (BOD), have their highest mean values of 6.00 ± 0.42 mg/L and 3.10 ± 0.41 mg/L respectively occurring in the well during the dry season, while the least value of DO (4.20 ± 0.71 mg/L) was found in the borehole in the dry season, but that of BOD (1.93 ± 0.55 mg/L) was recorded in the well during the wet season (Table 3). There was no significant difference in the values of DO as well as the BOD across the water bodies respectively (Table 3). DO level is an indication of the amount of oxygen in a body of water, and it is affected by pressure, temperature and salinity [35]. Higher DO in well during the dry season observed in this study maybe due to two reasons. One is diffusion of oxygen from surrounding air, as the sampled wells are shallow and frequently exposed to air when opened to draw water from them. Second reason is nutrient pollution, which result from decayed plants and animals, animal manure and storm run-off which move in to the soil and subsequently ground water. Excess DO in water bodies can cause emphysema (external bubbles), a rare condition that affects the skin and other tissues [35]. BOD is the amount of DO needed by aerobic biological organisms to break down OM present in a given water sample at certain temperature over a specific time period. Reference [36], stated that BOD is used as an indication of

the OM quality of water. BOD is affected by temperature, concentration of nutrients and available enzymes for the microbial populations. Also, the amount and activity of microorganisms have significant impact on BOD values. When the amount of microorganisms is small, the processes of biochemical breakdown do not occur, or the intensity of biochemical breakdown is insignificant [37]. In natural conditions, such effect is often caused by the presence of toxic inorganic substances (such as heavy metals) that adversely affect the enzymatic activity of the microorganisms. Under that circumstance, it must be considered that the changed values of BOD do not reflect the actual level of water pollution [37].

Table 3 also showed that organic matter (OM) and total organic carbon (TOC) had their highest mean values of 5.34 ± 0.97 mg/L and 3.11 ± 0.56 mg/L respectively occurring in the borehole during the wet season, while their least values of 2.52 ± 0.58 mg/L and 1.46 ± 0.34 mg/L respectively were obtained in the borehole in the dry season. There was a significant difference (P<0.05) in OM and TOC respective values in the water bodies (Table 3). TOC is the measurement of organic carbons in water, and it is often used as a non-specific indicator of water quality. TOC is also considered as the most relevant parameter for quantifying organic pollution in water [38]. Periodic

fluctuations in TOC concentrations may result from seasonal changes of groundwater level, which means that increased values of this parameter correspond to lower groundwater levels [37].

Seasonal fluctuations of this indicator can be attributed to runoff from the compostory plant and seasonal changes of groundwater level [37]. OM consists of organic compounds from the remains of dead organisms such as plants and animals, and their waste products in the environment [39]. As the OM moves in the environment (soil and water), microorganisms in the environment feed on the organic compounds. Changes in pH can affect the microorganisms that consume the organic matter and then affect the level of pollution caused by organic compounds [37]. From all of the above discussions, the availability and roles of DO, BOD, OM and TOC in water quality cannot be over emphasized.

From Table 3, highest mean values of Ca<sup>2+</sup> (26.31 ± 5.64 mg/L), Na<sup>+</sup> (11.30 ± 2.11 mg/L) and K<sup>+</sup> (8.85 ± 1.93 mg/L) occurred in the well water samples during the wet season, while the highest mean value of Mg<sup>2+</sup> (1.84 ± 0.30 mg/L) was obtained in the borehole during the dry season. The least values of Mg<sup>2+</sup> (1.32 ± 0.37 mg/L) and K<sup>+</sup> (5.74 ± 1.26 mg/L) were found in the borehole in the wet season, while Ca<sup>2+</sup> had its least value of 16.37 ± 3.67 mg/L also occurring in the borehole, but in the dry season. Na<sup>+</sup> has least value of 6.18 ± 2.50 from the well water samples during the dry season (Table 3). There was no significant difference in the values of the respective cations listed above across the water bodies (Table 3). Ca<sup>2+</sup> and Na<sup>+</sup>

values obtained in this study were below the national permissible levels, while Mg<sup>2+</sup> level was higher than the national standard. However, there is no report that higher magnesium level has any effect on human health [27]. The highest mean values of SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> were 14.44 ± 2.92 mg/L and 16.08 ± 2.28 mg/L respectively in the well water samples during the wet season, while the least values of 7.71 ± 1.65 mg/L and 8.91 ± 1.46 mg/L were obtained in the borehole samples in the wet season (Table 3). For Cl<sup>-</sup>, there was significant difference (P<0.05) across the water bodies, while for SO<sub>4</sub><sup>2-</sup>, there was no significant difference (Table 3). The highest value of NO<sub>3</sub><sup>-</sup> (5.80 ± 0.37)mg/L was found in the well water samples in the dry season, while the least value of 4.13 ± 0.40 mg/L was obtained in the borehole in the wet season (Table 3). A highly significant difference (P<0.01) in the values of NO<sub>3</sub><sup>-</sup> were obtained across the water bodies. The higher Cl<sup>-</sup> concentration obtained in the wet season in this study agrees with the finding of [40] who also reported higher Cl<sup>-</sup> level in wet season, and attributed it to industrial waste and/or leaching from upper soil layers. Also, higher SO<sub>4</sub><sup>2-</sup> value found during the wet season was supported by the findings of [41] who reported higher level of sulphate in wet season as well, and attributed it to action of leaching and release of sulphur gases from industries and utilities, which get oxidized. The levels of the three anions were below the national standards and international standards as at the time of this study, hence, they do not pose any threat to human health. However, one cannot rule out the possibility of increase over time due to accumulation in different matrices.

**Table 4. SEASONAL VARIATION IN HEAVY METALS OF WATER SAMPLES IN THE WATER BODIES**

Parameters (mg/L)	Borehole		Well		Overall mean		F	P	NSDWQ	WHO
	Wet	Dry	Wet	Dry	Wet	Dry				
<b>Cd</b>	0.088 ± 0.003 <sup>a</sup>	0.093 ± 0.0043 <sup>a</sup>	0.089 ± 0.002 <sup>a</sup>	0.086 ± 0.0028 <sup>a</sup>	0.089 ± 0.002	0.093 ± 0.004	.430	.912	0.003	0.003
<b>Cr</b>	0.0001 ± 0.006 <sup>a</sup>	0.006 ± 0.0032 <sup>a</sup>	0.09 ± 0.05 <sup>b</sup>	0.0028 ± 0.0068 <sup>a</sup>	0.002 ± 0.004	0.005 ± 0.002	2.726	.013*	0.05	0.05
<b>Fe</b>	0.34 ± 0.031 <sup>a</sup>	0.69 ± 0.05 <sup>a</sup>	0.27 ± 0.036 <sup>a</sup>	0.59 ± 0.043 <sup>a</sup>	0.33 ± 0.02	0.68 ± 0.03	6.223	.000***	0.3	NG
<b>Mn</b>	0.052 ± 0.004 <sup>a</sup>	0.089 ± 0.0031 <sup>a</sup>	0.18 ± 0.13 <sup>a</sup>	0.082 ± 0.0042 <sup>a</sup>	0.052 ± 0.003	0.090 ± 0.0024	.733	.677	0.20	0.50
<b>Zn</b>	0.080 ± 0.0067 <sup>a</sup>	0.084 ± 0.0091 <sup>a</sup>	0.11 ± 0.012 <sup>a</sup>	0.085 ± 0.01 <sup>a</sup>	0.085 ± 0.005	0.086 ± 0.01	.668	.733	3.0	3.0
<b>Pb</b>	0.098 ± 0.047 <sup>abc</sup>	0.24 ± 0.03 <sup>c</sup>	0.012 ± 0.0086 <sup>a</sup>	0.17 ± 0.025 <sup>bc</sup>	0.092 ± 0.025	0.24 ± 0.02	4.190	.001**	0.01	0.01

0.05=\* Significant difference; P<0.01=\*\* Highly significant difference; P<0.001=\*\*\* Very highly significant difference; Mean values with the same alphabets as superscripts along the rows are not statistically significantly different; NG = No Guideline; NSDWQ, 2007 = Nigeria Standard for Water Quality.

**Table 5. MAJOR IONS DOMINANCE IN SAMPLING STATIONS INVESTIGATED**

Station	Cationic Order	Anionic Order
<b>1 (Awosun Well 1)</b>	Ca <sup>2+</sup> >Na <sup>+</sup> >K <sup>+</sup> >Mg <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup> >Cl <sup>-</sup> >SO <sub>4</sub> <sup>2-</sup> >NO <sub>3</sub> <sup>-</sup>
<b>2 (Awosun Well 2)</b>	Ca <sup>2+</sup> >Na <sup>+</sup> >K <sup>+</sup> >Mg <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup> >SO <sub>4</sub> <sup>2-</sup> >Cl <sup>-</sup> >NO <sub>3</sub> <sup>-</sup>
<b>3 (Coker Borehole)</b>	Ca <sup>2+</sup> >Na <sup>+</sup> >Mg <sup>2+</sup> >K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup> >Cl <sup>-</sup> >SO <sub>4</sub> <sup>2-</sup> >NO <sub>3</sub> <sup>-</sup>
<b>4 (Fashina Borehole)</b>	Na <sup>+</sup> > Ca <sup>2+</sup> >K <sup>+</sup> >Mg <sup>2+</sup>	Cl <sup>-</sup> >HCO <sub>3</sub> <sup>-</sup> > SO <sub>4</sub> <sup>2-</sup> >NO <sub>3</sub> <sup>-</sup>
<b>5 (Ogunwusi Borehole)</b>	Ca <sup>2+</sup> >Na <sup>+</sup> >K <sup>+</sup> >Mg <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup> >SO <sub>4</sub> <sup>2-</sup> >Cl <sup>-</sup> >NO <sub>3</sub> <sup>-</sup>
<b>Total sample</b>	Ca <sup>2+</sup> >Na <sup>+</sup> >K <sup>+</sup> >Mg <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup> >Cl <sup>-</sup> >SO <sub>4</sub> <sup>2-</sup> >NO <sub>3</sub> <sup>-</sup>
<b>Wet season</b>	Ca <sup>2+</sup> >Na <sup>+</sup> >K <sup>+</sup> >Mg <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup> >Cl <sup>-</sup> >SO <sub>4</sub> <sup>2-</sup> >NO <sub>3</sub> <sup>-</sup>
<b>Dry season</b>	Ca <sup>2+</sup> >Na <sup>+</sup> >K <sup>+</sup> >Mg <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup> >Cl <sup>-</sup> >SO <sub>4</sub> <sup>2-</sup> >NO <sub>3</sub> <sup>-</sup>

Heavy metals such as Cd, Fe and Pb were observed to have high values of  $0.093 \pm 0.0043$  mg/L,  $0.69 \pm 0.05$  mg/L and  $0.24 \pm 0.03$  mg/L respectively in the borehole samples during the dry season (Table 4). Also from Table 4, it could be seen that the least value of Cd ( $0.086 \pm 0.0028$  mg/L) was found in the well during the dry season, while the least values of Fe ( $0.27 \pm 0.036$  mg/L) and Pb ( $0.012 \pm 0.0086$  mg/L) occurred in the well during the wet season. Cd showed no significant difference across the water bodies (Table 4). Lead (Pb) showed high significant difference ( $P < 0.01$ ), while Fe showed very high significant difference ( $P < 0.001$ ) across the water bodies (Table 4). The higher value of Pb in the dry season recorded in the borehole for this study is not in agreement with the finding of [17] who reported higher Pb concentration in borehole during the wet season. The difference in the results may be due to variation in the geology of the different study areas, and diversity in human activities occurring in the areas. However, it can be deduced that the water bodies are polluted with lead because both the highest and least values recorded in this study were above the national and international permissible levels. Pb is quite deadly and it can result in several diseases which are harmful to the human health especially children. The presence of Pb above the normal threshold results in carcinogenic diseases, interference with vitamin D metabolism and it affects mental development in infants [28,32]. For Fe, the higher concentration in the dry season obtained in this study agrees with the finding of [43] who also reported significant increase in the dry season concentration of Fe in soil around a Scrap Metal Recycling Factory, and attributed it to the activities of the factory, because most of the scraps were made from Fe and Al materials. The concentration of Fe detected in this study was quite higher than the national permissible level, and it may cause rapid increase in pulse rate and coagulation of blood in blood vessels, hypertension and drowsiness [44,45]. Cadmium's concentration recorded in this study was also significantly higher than the national and international standards. Cd enters into the environment when it is discharged as a by-product of the refining of Zinc, and do not degrade in the environment to products that are less toxic; hence they tend to bioaccumulate in the kidneys and livers of animals [46,47]. Reference [48] posited that as cadmium bioaccumulates over time, if not attended to it may cause kidney and liver failures in the people that consume water from the ground water sources. Cd exposure causes kidney damage, by interfering with enzymatic processes involving reabsorption of proteins in the kidney; and also causes hypertension [17,48]. For Cr, Mn and Zn, the highest mean values of  $0.09 \pm 0.05$  mg/L,

$0.18 \pm 0.13$  mg/L and  $0.11 \pm 0.012$  mg/L respectively were obtained in the well during the wet season, while the least values of  $0.0001 \pm 0.006$  mg/L,  $0.052 \pm 0.004$  mg/L and  $0.080 \pm 0.0067$  mg/L respectively, were recorded in the borehole during the wet season (Table 3). Cr showed significant difference ( $P < 0.05$ ), while both Mn and Zn showed no significant difference across the water bodies. Reference [49] studied the physicochemical properties of soil within the vicinity of an iron smelting factory, and also observed higher values of Cr and Zn in the wet season, which they stated may be due to easy availability of these metals during the rainy season than during the dry season. Soluble and unabsorbed chromium complexes can leach from soil into groundwater [50]. The higher Mn concentration in the well water found in this study may be due to the presence of Mn-containing materials deposited on the soil as a result of anthropogenic activities as reported by [51] who reported that anomalously high trace element found in the soil may be attributed to anthropogenic activities which may have seeped into the ground over time. The finding of this study was in agreement with [52], who reported higher level of Mn, though during the dry season, and attributed this to metal manufacturing industries, fertilizers and wastes.

The mean concentration of the cations in the overall samples during wet season and dry seasons were found to be in the order  $Ca^{2+} > Na^{+} > K^{+} > Mg^{2+}$  (Table 5). The same cationic order mentioned above occurred in stations 1, 2 and 5 (Awosun Well 1, Awosun Well 2 and Ogunwusi Borehole respectively) (Table 5). A different cationic order  $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$  occurred in Station 3 (Coker Borehole) and Station 4 (Fashina Borehole)  $Na^{+} > Ca^{2+} > K^{+} > Mg^{2+}$  as presented in Table 5. The anionic order of mean concentration in sampling stations 2 and 5 (Awosun Well 2 and Ogunwusi Borehole respectively) is  $HCO_3^{-} > SO_4^{2-} > Cl^{-} > NO_3^{-}$ , while it is  $HCO_3^{-} > Cl^{-} > SO_4^{2-} > NO_3^{-}$  in sampling stations 1 and 3 (Awosun Well 1 and Coker Borehole respectively) (Table 5). Also, from Table 5, sampling station 4 (Fashina Borehole) showed a totally different anionic order  $Cl^{-} > HCO_3^{-} > SO_4^{2-} > NO_3^{-}$ . The anionic order in the overall samples, in dry season and wet seasons is  $HCO_3^{-} > Cl^{-} > SO_4^{2-} > NO_3^{-}$  as shown in Table 5. However, [53] recorded the sequence  $K^{+} > Na^{+} > Ca^{2+} > Mg^{2+}$  for cations and  $Cl^{-} > HCO_3^{-} > SO_4^{2-} > F^{-}$  for anions in their study of irrigation and drinking water quality index determination for groundwater quality evaluation in Akoko, Ondo State Nigeria. Our results on these physicochemical properties of ground waters in the study area are in line with that of [54] who reported that anthropogenic activities do impact the physicochemical properties of groundwater.

**Table 6. IONIC ERROR OF BALANCE (IEB) (%) OF VALUES OF MAJOR CATIONS AND ANIONS OF THE WATER BODIES**

STATIONS	Cations (meq <sup>l</sup> <sup>-1</sup> )				Sum of Cations	Anions (meq <sup>l</sup> <sup>-1</sup> )				Sum of Anions	% IEB
	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>		Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>		
Awosun Well 1	1.279952	0.12821	0.489013	0.16512	2.06	0.587427	0.27496	0.6888	0.094738	1.65	11.05
Awosun Well 2	0.875229	0.132915	0.27115	0.255787	1.54	0.278592	0.30035	0.62976	0.078732	1.29	8.83
Coker Borehole	1.705532	0.151871	0.40745	0.091733	2.36	0.362495	0.18956	1.6892	0.079399	2.32	0.85
Fashina Borehole	0.762522	0.146261	0.9744	0.412928	2.30	0.883767	0.28188	0.59696	0.098739	1.86	10.58
Ogunwusi Borehole	0.697785	0.109363	0.630388	0.189227	1.63	0.223251	0.22418	0.8856	0.071396	1.40	7.59
Total	1.064180	0.133724	0.5544802	0.222959	1.98	0.467106	0.25419	0.89806	0.084601	1.70	7.61

$$\% \text{ IEB} = \{(\sum \text{cations} - \sum \text{anions}) \div (\sum \text{cations} + \sum \text{anions})\} \times 100 \text{ (Huh et. al., 1998).}$$

Table 6 showed the percentage ionic error balance (IEB) of values of major cations and anions in the investigated water bodies. Ionic balance of groundwater has also been done for a quality-assurance check of the chemical analyses. According to standard rules, the ion balance of a fresh water sample with low TDS is considered to be good if the value is between  $-10\%$  and  $+10\%$  [55,56].

## 4. Conclusion

This study has been able to document the physicochemical quality of groundwater bodies around an Iron and Steel Recycling Industry and assessed the impact on water bodies. Most of the detected parameters did not exceed the national and international standard except turbidity, dissolved oxygen, and heavy metals like cadmium, lead and iron which significantly exceeded the national and international standards. These high levels may pose serious health risks to people who drink the water and gives cause for concern. The Iron and Steel Recycling Industry might have contributed to the high levels of these heavy metals in addition to the natural content of the soil. Lastly, this study has provided baseline information on the physicochemical properties of groundwater bodies around the Iron and Steel Recycling Industry. It is highly suggested that frequent monitoring should be carried out for parameters such as turbidity, and heavy metals like Cd, Fe and Pb concentrations in the study area.

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