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Full Length Research Paper

Assessment of ground water pollution in the residential areas of Ewekoro and Shagamu due to cement production

Temilola Oluseyi[1], Kehinde Olayinka[1] and Ismaila Adeleke[2]*

[1]Department of Chemistry, University of Lagos, Nigeria.
[2]Department of Actuarial Science, University of Lagos, Nigeria.

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Chemical and physico–chemical parameters of ground water samples from wells were analyzed by multivariate statistical tools to provide the characterisation of the ground water distribution of the settlements around cement factories in Ewekoro and Shagamu, Ogun State in Nigeria. The 17 parameters determined include: pH, conductivity, dissolved oxygen (DO), total dissolved solids (TDS), biochemical oxygen demand (BOD), total hardness, acidity, and alkalinity; anions such as chlorides, sulphates, phosphates and nitrates as well as potentially toxic metals such as copper, lead, zinc, iron and cadmium. The analytical data were obtained from 6 wells in Ewekoro and 11 wells in Shagamu sampled during three different periods along a year covering both the wet, break and dry seasons of 2009. The concentrations of lead and cadmium are above the World Health Organisation (WHO) standard in all three seasons investigated with lead having as high as 1.05 mg/L and maximum of 0.068 mg/L for cadmium. It was also observed that the levels of sulphate was higher that the WHO standard during the dry season with a maximum concentration of 623 mg/L. All other physicochemical parameters fell within the permissible range as stipulated by the WHO. There was no seasonal difference in the concentrations of the potentially toxic metals analysed in the ground water from the two sites, while for the physicochemical properties, there was a seasonal variation in the results of the ground water quality in the two sites studied with DO having a p-value of 0.009, BOD with p-value of 0.04 and Alkalinity of 0.044 p-value. An approach for the characterisation of the groundwater system of the neighbourhood of the cement factories is proposed on the basis of its physico-chemical composition, in order to detect multivariate patterns for unpolluted waters as well as for eventual polluted zones.

Key words: Toxic metals, physico-chemical composition, multivariate, cement, ground water.

INTRODUCTION

Groundwater is a vital natural resource for the reliable and economic provision of potable water supply in both the urban and rural environment. Worldwide, aquifers that is, geological formations containing usable groundwater resources are experiencing an increasing threat of pollution from urbanization, industrial development, agricultural and mining activities. Thus necessitating extensive study of the quality of groundwater leading to proactive campaigns and practical actions to protect the natural quality of groundwater is widely required. In Nigeria, a large part of drinking water supply is by ground water through dug wells and bore holes. In many of the rural areas and part of the urban areas too, ground water is only source of drinking water, thus a large population is exposed to risk of consuming contaminated water. Groundwater quality depends not only on natural factors such as aquifer lithology, groundwater velocity, quality of recharge waters and interaction with other types of water or aquifers, but also on human activities and the environment. The environment plays an important role in health and human development, and the acute effects

*Corresponding author. E-mail: adeleke22000@yahoo.ca, iadeleke@unilag.edu.ng.

from exposure to environmental contaminants is linked to specific environmental hazards with a health effect, such as benzene and leukaemia. Examining time trends in environmental hazard can be helpful in understanding background and changes in environmental contamination.

Cement industries are generally associated with high dust emissions into the atmosphere. Emitted dusts are naturally eliminated as deposits to the earth surface through dry or wet deposition in rainfall (Olaleye, 2005; Asubiojo et al., 1991). The damaging consequences of the released dust particles for the soil, flora and fauna of the cement factory neighbourhood could be considerable (Akeredolu, 1989) and the damaging effects of dust particles have been attributed to the cement dust fall, which is characterized by enriched toxic heavy metals such as arsenic, lead, nickel, chromium, copper, zinc, manganese and cadmium (Olaleye, 2005; Adejumo et al., 1994).

Groundwater quality comprises the physical, chemical, and biological qualities of ground water. Temperature, turbidity, colour, taste, and odour make up the list of physical water quality parameters. Since most ground water is colourless, odourless, and without specific taste, the concern is the chemical qualities. Specific areas of interest are to study the spatial and seasonal variation in the quality of ground water. Naturally, ground water contains mineral ions and these ions slowly dissolve from soil particles, sediments, and rocks as the water travels along mineral surfaces in the pores or fractures of the unsaturated zone and the aquifer. Some dissolved solids may have originated in the precipitation water or river water that recharges the aquifer. However, human activities can alter the natural composition of ground water through mining activities, the disposal or dissemination of chemicals and microbial matter at the land surface and into soils, or through injection of wastes directly into ground water.

Some statistical techniques had been used to provide insight to the complexity and abundances of interactions in a surface water system that is very difficult to obtain: techniques such as multivariate statistical techniques and mathematical models. Multivariate analyses, such as cluster, factor and discriminant analysis are aimed at interpreting the governing processes through data reduction and classification and they are widely applied to spatial data in geochemistry (Papatheodorou et al., 2001, 2002, 2004), hydrochemistry (Voudouris et al., 1997; Lambrakis et al., 1997), mineralogy and even in marine geophysics. The application of these techniques to water quality monitoring and assessment has increased in recent studies lead to appreciable data analysis and decisions (Lambrakis et al., 1997). The multivariate treatment of environmental data is widely used to characterise and evaluate surface and freshwater quality, and it is useful for evidencing temporal and spatial variations caused by natural and human factors linked to seasonality (Elosegui and Pozo, 1994; Grimalt et al., 1990). However, in this study, the seasonal variations of the physicochemical properties as well as some polluting sources, such as those derived from cement production activities, on the groundwater in the neighbourhood was studied. The analysis of variance technique (ANOVA) was used to measure significant effects of season on the concentration of physicochemical properties of groundwater. The ANOVA tests would be able to assess the seasonal effects on these parameters. In its simplest form ANOVA provides a statistical test whether or not the means of several groups are all equal, and therefore generalizes Student's two-sample *t*-test to more than two groups. A statistically significant effect in ANOVA is often followed up with one or more different follow-up (post hoc) tests.

The remainder of the article is structured as follows: First is a description of the materials used in the study as well as the statistical techniques used in analysis, whilst the results are next discussed. This is followed by conclusion and policy recommendations.

MATERIALS AND METHODS

Study area

Ewekoro cement production facility located five kilometres North of Ewekoro town (6º55′ N 3º12′ E) is within the tropical rainforest belt of Nigeria. Farming settlements such as Olapeleke (West), Itori (North), Elebute and Alaguntan (East) which predate the factory are locate within 10 km radius of the production facility (Olaleye, 2005). The Ewekoro cement production facility of the West African Portland Cement (WAPC) PLC established in 1959 is the oldest cement factory in Nigeria. The annual cement production from the factory using wet and semi-wet clinker production technology varied between 254,000 and 479,000 metric tonnes (WAPC, 2000).

Lafarge Cement WAPCO Nigeria PLC formerly WAPCO was established in 1959 with its first factory in Ewekoro, Ogun State in 1960. The second factory in Sagamu, also in Ogun State was established in 1978. The Company commenced production with an initial capacity of 200,000 tonnes per annum, but this later grew with demand to about 1.5 million metric tonnes per annum (Lafarge in Nigeria, 2009) (Figure 1).

Sampling

The water samples were collected in pre washed plastic containers for most of the analysis. Samples for the determination of dissolved oxygen were collected in 250 ml air tight DO glass bottles and immediately the oxygen was fixed with 2 ml prepared alkali-iodide-azide solution. Samples were stored in the refrigerator before laboratory analysis which was carried out within one week of sample collection while analysis of dissolved oxygen (DO) and biochemical oxygen demand (BOD) were carried out the same day the samples were collected.

Sample analysis

The following physico-chemical parameters were determined, pH, total hardness, total dissolved solids, chlorides, dissolved oxygen, biochemical oxygen demand, conductivity, acidity, alkalinity,

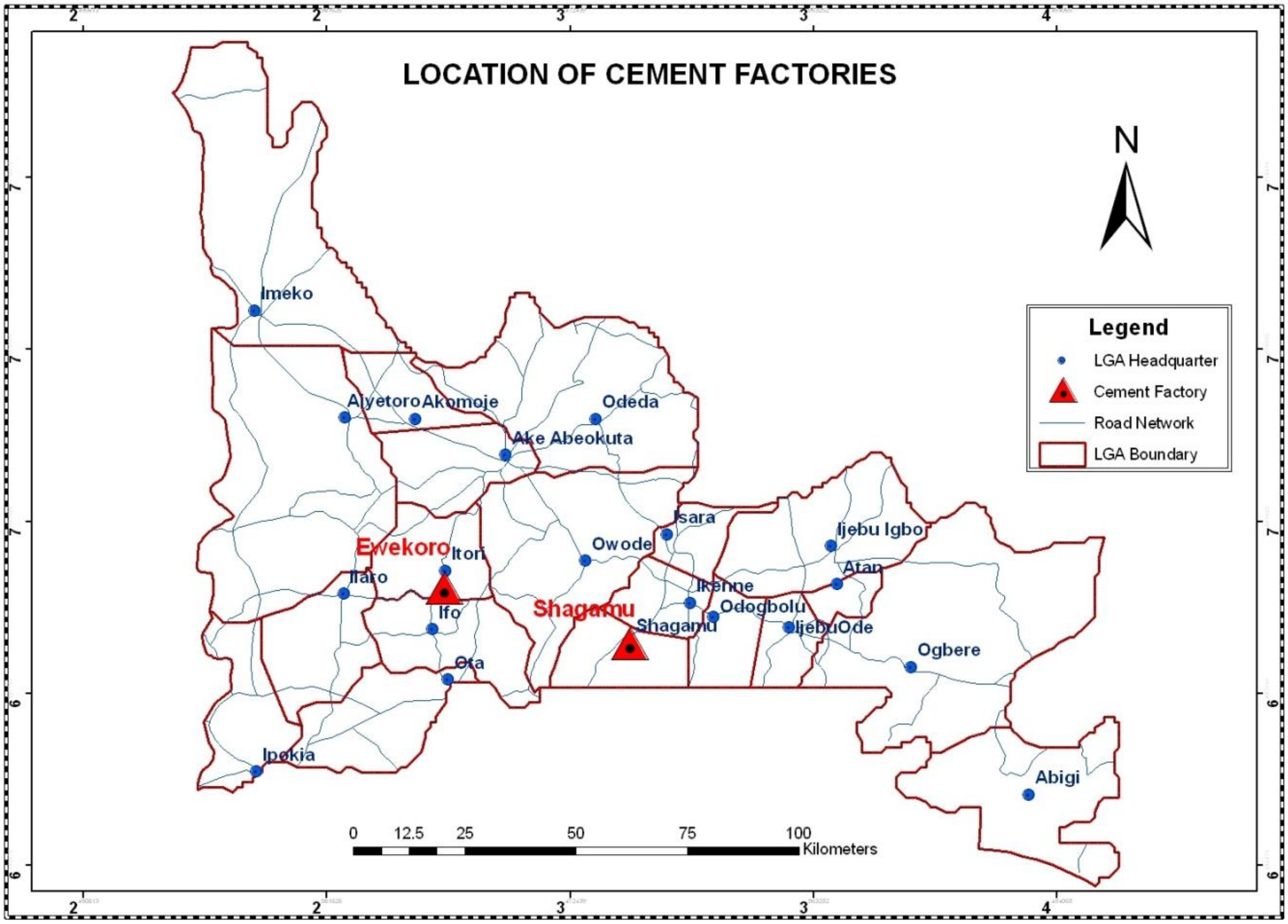

Figure 1. Map showing the sampling area**.**

sulphates, phosphates, nitrates. Also heavy metals such as copper, Iron, zinc, cadmium and lead were determined using standard methods. The adopted methods for determining the physico-chemical parameters are listed in Table 1.

Statistical analysis

In this study, the analysis of variance technique (ANOVA) was used to measure significant effects of season on the concentration of physicochemical properties of groundwater. Analysis of variance is used to test the hypothesis that several means are equal (Strang, 2009). This technique is an extension of the two-sample t test. In addition to determining that differences exist among the means, you may want to know which means differ (Bailey, 2008; Klaus and Oscar 2008). The ANOVA model for this design is:

$$Y_{ij} = \mu + \tau_j + \varepsilon_{ij} \quad (1)$$

where Y_{ij} represents the i^{th} observation (i = 1, 2, . . ., n_j) on the j^{th} season (j = 1, 2, 3). μ is a common effect for the whole experiment, τ_j represents the effect of the j^{th} season, and ε_{ij} represents the random error present in the i^{th} observation (i = 1, 2, . . ., n_j) on the j^{th} season. The statistical analysis is designed to identify whether the mean result (concentration of parameters) from all Subseason of data (that is, season) are homogeneous. If the F ratio is highly significant, one concludes that season indeed has a strong effect on the measured parameters. However, since the season factor is at quantitative levels and these levels are equispaced (that is about three months apart), one might suspect some functional relationship between some or probably all the parameters and season. If such a relationship can be found, the concentration of parameter concerned can be predicted from season. In seeking a model for the relationship between Y_{ij} and the season (call it X_j), as a first approximation, a linear regression model would be:

$$Y_{ij} \equiv \mu + \left(\mu_{y/x} - \mu\right) + \left(\mu_{\cdot j} - \mu_{y/x}\right) + \left(Y_{ij} - \mu_{\cdot j}\right) \quad (2)$$

where μ is the effect of the overall mean, $\mu_{y/x}$ represents the predicted mean of Y for each X, based on the model considered, $\mu_{\cdot j} - \mu_{y/x}$ represents the departure of the treatment (season) means from the regression model, and $Y_{ij} - \mu_{\cdot j}$ is the error within each treatment. If there are no regression models involved, the second and third expressions on the right combine to give $\mu_{\cdot j} - \mu$

Table 1. Analytical methods applied for the determination of physico-chemical parameters.

Parameter	Unit of measurement	Analytical method
pH		Potentiometry
Conductivity	µs/cm	Conductimetry
Total hardness	$Mgcaco_3$/L	Titrimetry
Total dissolved solids (TDS)	mg/l	Gravimetry
Dissolved oxygen (DO)	Mgo_2/L	Titrimetry
Biochemical oxygen demand (BOD)	Mgo_2/L	Titrimetry
Acidity	$Mgcaco_3$/L	Titrimetry
Alkalinity	$Mgcaco_3$/L	Titrimetry
Chlorides (Cl^-)	Mg/L	Titrimetry
Sulphates (SO_4^{2-})	Mg/L	Spectrophotometry
Phosphates (PO_4^{3-})	Mg/L	Spectrophotometry
Nitrates (NO^{3-})	Mg/L	Spectrophotometry
Copper (Cu)	Mg/L	Atomic absorption spectrometry
Iron (Fe)	Mg/L	Atomic absorption spectrometry
Zinc (Zn)	Mg/L	Atomic absorption spectrometry
Cadmium (Cd)	Mg/L	Atomic absorption spectrometry
Lead (Pb)	Mg/L	Atomic absorption spectrometry

or τ_j which is the ANOVA model.

When the sample estimates are substituted in this model,

$$Y_{ij} = \bar{Y}_{..} + (Y'_x - \bar{Y}_{..}) + (\bar{Y}_{.j} - Y'_x) + (Y_{ij} - \bar{Y}_{.j}) \quad (3)$$

For a straight-line model,

$$Y'_x = b_0 + b_1 X_j \quad (4)$$

Where b_0 is the intercept and b_1 the slope. To determine b_0 and b_1 the method of least squares is used.

RESULTS AND DISCUSSION

Descriptive data analysis

The results of the descriptive statistics of each data set are given in Tables 2 to 5. The values of the mean, median, standard deviation, minimum and maximum concentrations of the physico chemical parameters (both metals and non-metals) are presented. The median values which are not affected by extreme values were taken into consideration as characteristics values to see the differences in the three different seasons from the two sites.

The results of the physicochemical analysis for the waters samples from the various wells in the neighbourhood of Ewekoro Cement factory are as shown in Table 3. The levels of phosphate, nitrate and chloride were generally below the World Health Organization (WHO) and Nigerian standard for drinking water quality (NSDWQ). However the pH values were found to be below the standard regulatory values especially during the dry season, as the water samples were found to be acidic with a mean value of 5.2. Similarly the sulphate level was well above the WHO standard during the dry season with a mean concentration of 623 mg/L.

Table 3 shows the concentrations of the potentially toxic metals in the water samples. Some of their values exceeded the limit for drinking water. There was no obvious trend in the way the values varied from well to well. However it was observed that copper, iron and zinc were lower that the regulatory limit. Only lead and cadmium were found to exceed the regulatory limit for some wells. These might be due to other environmental factors like soil type or the proximity of these wells to the cement factories.

Table 4 shows the results of the physicochemical analysis of the water samples in Shagamu close to Lafarge Cement factory. Similar trends and patterns were observed for all the results with that of the samples obtained from Ewekoro. The levels of the alkalinity, conductivity, acidity, total dissolved solids, phosphate, nitrate and chloride were generally below the World Health Organization (WHO) and Nigerian standard for drinking water quality (NSDWQ). In contrast with the results obtained from underground water samples in Ewekoro, the minimum pH values were found to be lower the standard regulatory values during the three seasons investigated, as the water samples were found to be acidic with values of 5.8, 6.1 and 6.6 for wet, break and dry seasons respectively. Similarly the sulphate level was well above the WHO standard during the dry season with a mean concentration of 542 mg/L. The mean

Table 2. Descriptive statistics of parameters (Non metals) measured in Ewekoro.

Parameter	Descriptives	Season		
		Rain	Break	Dry
pH	Mean	6.5	7.2	5.2
	Minimum	5.2	6.1	-
	Maximum	7.5	8	8
Total hardness ($mgCaCO_3/L$)	Mean	121	159.25	117.25
	Minimum	64	56	-
	Maximum	222	236	270
TDS (mg/L)	Mean	16.59	23.99	15.26
	Minimum	1	-	-
	Maximum	43	65	55
Cl (mg/L)	Mean	36.39	39.94	19.53
	Minimum	21.3	7.1	-
	Maximum	56.8	63.9	56.8
DO (mgO_2/L)	Mean	6.77	8.60	4.82
	Minimum	5.3	6.3	-
	Maximum	10.6	10.6	8
BOD (mgO_2/l)	Mean	1.24	3.34	2.51
	Minimum	0.5	1.4	-
	Maximum	2.7	5.1	5.9
Conductivity (µs/cm)	Mean	432.38	597.75	306.5
	Minimum	266	285	-
	Maximum	884	1030	646
Acidity ($mgCaCO_3/L$)	Mean	3.44	4.05	3.94
	Minimum	0.6	2.4	-
	Maximum	7.1	8.1	9.4
Alkalinity ($mgCaCO_3/L$)	Mean	76.11	60.15	45.65
	Minimum	9.3	0.6	-
	Maximum	152.5	150.4	81
Sulphate (mg/L)	Mean	84.63	75.79	84.12
	Minimum	28.3	-	-
	Maximum	175	197	623
Phosphate (mg/L)	Mean	0.08	0.25	0.11
	Minimum	0.01	0.01	-
	Maximum	0.43	0.43	0.4
Nitrate (mg/L)	Mean	7.86	4.94	6.71
	Minimum	-	-	-
	Maximum	20.1	11.2	36

concentration of dissolved oxygen was found also to be lower than the standard regulatory values.

Table 5 shows the concentrations of the potentially toxic metals in the water samples. Similar trend was observed like the Ewekoro water samples. The concentrations of copper, iron and zinc in the water samples were found to lower that the regulatory limit. Only lead and cadmium were found to exceed the regulatory limit for some wells.

Analysis of variance

The results as presented in Tables 6 and 7 , suggest that there are no significant differences in metal concentrations in the sediment samples from the two

Table 3. Descriptive statistics of parameters (metals) measured in Ewekoro.

Parameter	Descriptives	Season		
		Rain	Break	Dry
Cu (mg/L)	Mean	0.0613	0.0438	0.0338
	Minimum	0.03	0.03	-
	Maximum	0.09	0.08	0.06
Fe ((mg/L)	Mean	0.0475	0.0325	0.0225
	Minimum	0.01	0.01	-
	Maximum	0.09	0.09	0.05
Zn (mg/L)	Mean	0.1975	0.225	0.1713
	Minimum	0.11	0.14	-
	Maximum	0.27	0.42	0.35
Cd (mg/L)	Mean	0.0374	0.0291	0.0308
	Minimum	0.01	0.01	-
	Maximum	0.07	0.05	0.08
Pb (mg/L)	Mean	0.882	0.989	0.7795
	Minimum	0.4	0.78	-
	Maximum	1.05	1.1	1.3

Table 4. Descriptive statistics of water quality parameters (Non-metals) measured in Lafarge.

Parameter	Descriptives	Season		
		Wet	Break	Dry
pH	Mean	6.7	7.4	7.3
	Minimum	5.8	6.1	6.6
	Maximum	8.1	8.1	8.1
Total Hardness (mgCaCO$_3$/L)	Mean	118.67	112.67	122.83
	Minimum	30	26	20
	Maximum	154	154	240
TDS (mg/L)	Mean	18.42	22.75	23.75
	Minimum	6	7	8
	Maximum	25	35	34
Cl (mg/L)	Mean	26.81	39.4	33.43
	Minimum	14.2	7	14
	Maximum	88.8	88.8	62.1
DO (mgO$_2$/L)	Mean	6.2	5.3	4.6
	Minimum	4	2.4	2.3
	Maximum	9.1	7.9	6.7
BOD (mgO$_2$/L)	Mean	36.8	33.4	49.2
	Minimum	2.7	5.5	8.5
	Maximum	112.9	109	112.9
Conductivity (µs/cm)	Mean	285.79	260.21	308.42
	Minimum	124	86	124
	Maximum	352	371	485

Table 4. Contd.

	Mean	4.95	4.99	5.2
Acidity (mg$CaCO_3$/L)4	Minimum	2.8	2.8	2.8
	Maximum	6.8	11.2	12.8
	Mean	99.33	64.92	79.67
Alkalinity (mg$CaCO_3$/L)	Minimum	21	20	25
	Maximum	159	104	112
	Mean	148.48	67.35	218.42
Sulphate (mg/L)	Minimum	2	12	11
	Maximum	395	202	542
	Mean	0.1053	0.2074	0.282
Phosphate (mg/L)	Minimum	0	0.01	0
	Maximum	0.48	0.53	1.15
	Mean	2.71	5.3	4.1
Nitrate (mg/L)	Minimum	0	1.8	0.1
	Maximum	10.3	18.7	8.4

Table 5. Descriptive statistics of water quality parameters (metals) measured in Lafarge.

Parameter	Descriptives	Season		
		Wet	Break	Dry
	Mean	0.10938	0.03424	0.04115
Cu (mg/L)	Minimum	0.024	0.024	0.022
	Maximum	0.859	0.06	0.057
	Mean	0.03674	0.03589	0.0338
Fe (mg/L)	Minimum	0.022	0.022	0.022
	Maximum	0.056	0.052	0.056
	Mean	0.16433	0.18058	0.1785
Zn (mg/L)	Minimum	0.077	0.071	0.075
	Maximum	0.245	0.245	0.266
	Mean	0.0402	0.0448	0.04283
Cd (mg/L)	Minimum	0.015	0.021	0.016
	Maximum	0.068	0.065	0.067
	Mean	0.9646	0.9119	0.9003
Pb (mg/L)	Minimum	0.76	0.74	0.7
	Maximum	1.04	1.04	1.04

Ewekoro there is no seasonal effect on the all parameters except for ph and sulphate in Lafarge however, similar trend was notice but the parameters that have seasonal effect are DO, BOD sulphate, and phosphate. Having revealed that there is a significant seasonal effect on pH, sulphate, DO, BOD and phosphate concentrations, the question naturally arise, "which seasons means differ?" that is, when are the concentrations high or low? To answer such question, the Duncan multiple range test was conducted to further investigate the source of difference. In Lafarge, results from the Duncan test suggest that the pH level in dry and break are similar but are significantly higher than the level in wet season. For Sulphate, concentration in break and wet seasons are similar (that is, concentration not significantly different), but the concentration in dry season is significantly higher than those of break and wet.

In Ewekoro, DO concentration in break and wet

Table 6. ANOVA with Linear and Second-Degree Regression of parameters in Ewekoro.

Location	Element	Source	Sum of squares	df	Mean square	F	P-value
Ewekoro	DO	Between season	56.984	2	28.492	5.965	0.009
		Linear	15.171	1	15.171		
		Quadratic	41.813	1	41.813		
		Within season	100.309	21	4.777		
		Total	157.294	23			
	BOD	Between season	17.759	2	8.879	3.778	0.04
		Linear	6.439	1	6.439		
		Quadratic	11.32	1	11.32		
		Within season	49.363	21	2.351		
		Total	67.121	23			
Lafarge	pH	Between season	3.526	2	1.763	4.237	0.023
		Linear	2.574	1	2.574		
		Quadratic	0.952	1	0.952		
		Within season	13.731	33	0.416		
		Total	17.258	35			
	Alkalinity	Between season	7155.389	2	3577.694	3.428	0.044
		Linear	2320.667	1	2320.667		
		Quadratic	48334.722	1	48334.722		
		Within season	34440.75	33	1043.659		
		Total	41596.139	35			
	Sulphate	Between season	137184.037	2	68592.019	4.124	0.025
		Linear	29357.246	1	29357.246		
		Quadratic	107826.761	1	107826.761		
		Within season	548911.513	33	16633.682		
		Total	686095.55	35			

Table 7. ANOVA with linear and second-degree Regression of parameters in Lafarge.

Element	Source	Sum of squares	Df	Mean square	F	P-value
pH	Between season	3.52635	2	1.763175	4.237337	0.023018
	Linear	2.574	1	2.574		
	Quadratic	0.952	1	0.952		
	Within season	13.73145	33	0.416105		
	Total	17.2578	35			
Sulphate	Between season	137184	2	68592.02	4.123682	0.025202
	Linear	29357.25	1	29357.25		
	Quadratic	107826.8	1	107826.8		
	Within season	548911.5	33	16633.68		
	Total	686095.6	35			

seasons are not significantly different. Though marginally, DO level in wet is higher than that of break. However the concentration in dry season is significantly higher than those of break and wet. BOD results from the Duncan test also suggest that the BOD concentration in dry and break are significantly higher than that of the wet season, although BOD concentration in dry and break season are similar. Results also revealed that in Ewekoro, sulphate level in break and wet seasons are not significantly different. However the concentration in dry season is significantly higher than those of break and wet. For Phosphate, results show a similar pattern with that of sulphate. The phosphate concentration in break and wet seasons are not significantly different. Phosphate level in wet is higher than that of break. However the concentration in dry season is significantly higher than those of break and wet.

Conclusion

The descriptive statistics of concentration of parameters, along with the analysis of variance test provide evidence that there is no seasonal difference in the concentrations of the metals tested in the two sites; Ewekoro and Lafarge. However, there are seasonal differences in DO, BOD, Sulphate and Phosphate concentrations in Ewekoro, while in Lafarge, only ph and sulphate differ from season to season. The test also suggests that in Ewekoro, average DO concentration in wet season is highest compared to dry and wet. This is followed by dry with break having the least. For BOD, the average concentration in wet season is the highest, followed by dry and then break. Sulphate has its highest concentration in break, next to it is wet with dry season having the least. Phosphate was found to be the same as that of sulphate.

In Lafarge, the pH reading in wet season is highest of the three seasons, followed by Break and then dry. Unlike Ewekoro, the concentration of sulphate is highest in dry season in Lafarge, next to it is wet season while the break season has the highest concentration of sulphate.

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