

## INFLUENCE OF MINING AND AGRICULTURAL ACTIVITIES ON THE QUALITY OF GROUNDWATER FROM SOME RURAL AREAS OF SOUTH-EASTERN NIGERIA

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### ABSTRACT

This study examined the trends in anthropogenic chemical contaminants in groundwater samples in rural areas of Ebonyi State, South-eastern Nigeria. Groundwater samples were collected from Ezza North (a quarry mining area) and Ezza South (an agricultural/commercial area) and were analysed using standard techniques. The target compounds evaluated were As(V), phosphate, nitrate, sulfate, chloride and other physicochemical parameters. Pearson's correlation and factor analyses were used to distinguish the statistical relationship between the various analytes and possible contamination sources in the study areas, respectively. The results obtained showed that the pH, temperature, total hardness, electrical conductivity, phosphate, nitrate, chloride and sulfate were within the permissible limits of Water Quality Standards (WQS). Also, 67% of the samples had turbidity and alkalinity values above the WQS, while 25% contained As(V) slightly above the WQS. The qualities of the groundwater samples were found to be influenced mainly by the geochemistry of the soil while commercial and agricultural activities were found to have slight effect on the water quality. This study finally advocates adequate monitoring of As(V), and other potential toxic contaminants in groundwater in the areas.

**Keywords:** groundwater, arsenic, chemical contaminants, mining area, factor analysis

### 1. Introduction

The Report of the British Geological Survey (Natural Environment Research Council) on Nigeria in 2005 recommended studies on groundwater quality with emphasis on the impacts of arsenic, fluoride and sanitation. This, according to the report, was because most of the rural people in Nigeria depended on groundwater supply, with over half not having access to safe and reliable water supply, which is vital for better health and poverty reduction (MacDonald *et al.*, 2005). In order to meet the Millennium Development Goals (MDGs) target of 2015, which is to reduce by half the number of people without access to safe reliable water supplies, it is imperative to monitor water sources for the levels of their chemical contaminants (Gómez *et al.*, 2012). However, many studies on the chemical contaminants of groundwater in Nigeria are focused mainly on total trace metal contents and other well-known contaminants, with little or no studies done on the levels of the speciated forms of metals (e.g. arsenic). Though, arsenic is present in the environment in a number of different inorganic and organic forms, due to its participation in complex biological and chemical processes (Villa-Lojo *et al.*, 2002), As(III/V) are the predominant in water. Under oxidizing conditions, As(V) predominates and is found in the common pH

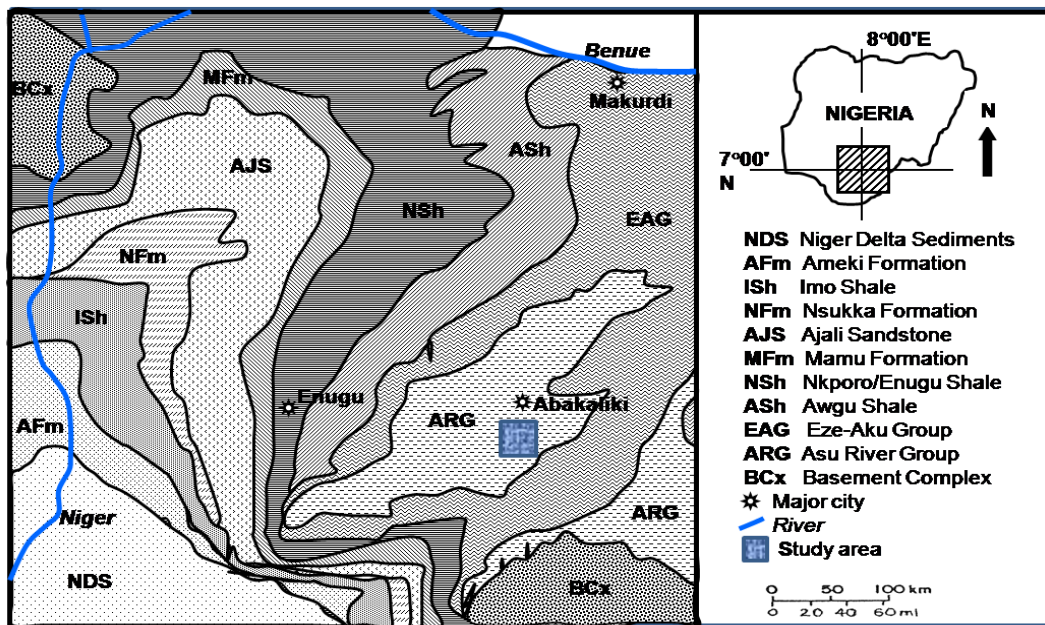
range of most natural ground- and surface waters as the oxyanions  $H_2AsO_4^-$  ( $pH < 6.8$ ) and  $HAso_4^{2-}$  ( $pH > 6.8$ ). In water with reducing conditions, As(III) is the predominant oxidation state while the neutral species  $H_3AsO_3$  predominates in water with  $pH < 9.2$  (Bundschuh *et al.*, 2012).

Thus, this study is aimed at examining the trends in chemical contaminants of groundwater sources of rural communities that are affected by mining and agricultural activities. As(V) was the major targeted chemical contaminant monitored. This was because of its inherent toxicity. It was also a least studied chemical contaminant in groundwater in the study area. However, other contaminants were studied to enable a wider discussion of the chemical water quality of the samples.

**2. Experimental Section**

*2.1. Background of the sampled area*

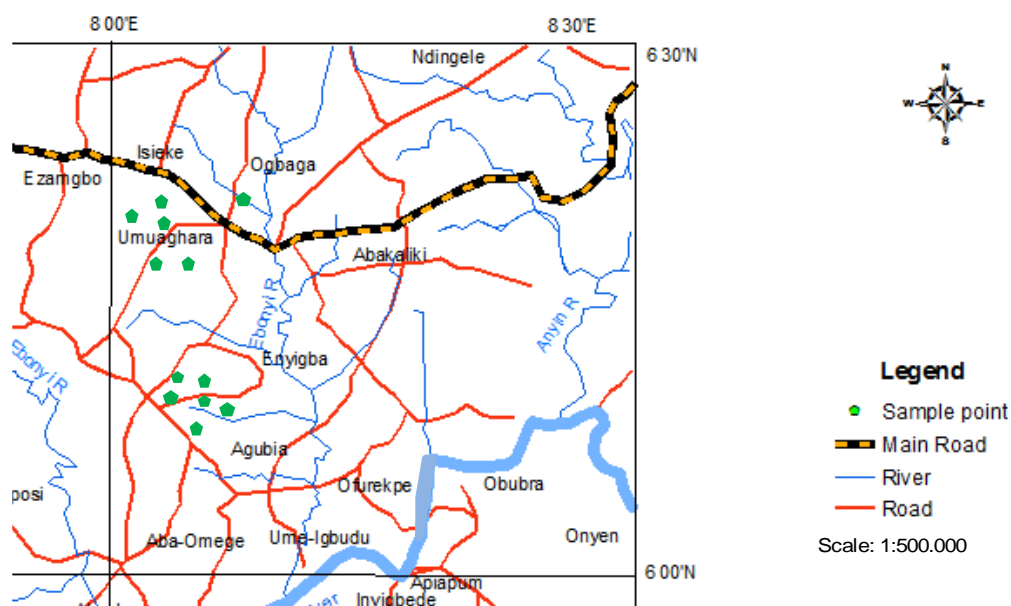
The study area is, geologically, underlain by the Asu River Group (Reyment, 1965), as shown in Figure 1. The Asu River Group sediments are predominantly shales, and with localized occurrences of sandstone, siltstone and limestone intercalations. This group was generally believed to have started depositing in the mid-Albian period and was deposited within the lower (or southern) Benue Trough, South-eastern Nigeria. It has an average thickness of about 5000 m, and was dark grey in colour but was weathered to brownish clayey shale or laterites in the greater part of the formation. The group is deeply folded, faulted and fractured by the series of tectonic activities which has acted on the rocks (Ezeh and Anike, 2009). This has given the shales the ability to house groundwater at economic quantity in some areas. The major part of the area is underlain by aquiclude; except in locations or zones where secondary aquiferous conditions were made possible by syn- and post depositional circumstances. The syn-depositional circumstance is the occurrence of lenses of sandstone or siltstone beds, while the post depositional circumstances include weathering, fracturing or shearing, and volcanic intrusions. The zones are recharged mostly in the peak of rainy season and by surface waters in the area.



**Figure 1.** Geological map of South-eastern Nigeria showing the study area

The study area is bounded by latitude  $6^{\circ} 09^1$  to  $6^{\circ} 14^1$  N, longitude  $8^{\circ} 05^1$  E to  $8^{\circ} 10^1$  E (Figure 2). The sampled points in Ezza South are around Onueke which is about 23 km south of Abakaliki metropolis, while the points in Ezza North are about 4 – 6 km from Abakaliki metropolis. The area falls within the rainforest climatic region of South-Eastern Nigeria where the rainy season spans from April to October and the dry season from October to April. The average annual rainfall of the study area is about 1500 mm

with actual surface temperature (seasonal temperature) of between 24-36 °C during dry season and about 18 °C during the rainy season. The study area is of high leached red soils of tropical forest areas with the vegetation dominated by grasses, shrubs and trees e.g. palm trees, coconut, mango, and orange trees (Omaka *et al.*, 2014). The major occupation of the people living in the area is farming (Ezza South) and mining activities (Ezza North). Pb-Zn mining and quarrying for construction work are secondary occupations to the people (Nnabo *et al.* 2011).



**Figure 2.** Map of the study area showing the sample points

## 2.2. Analytical methods

### 2.2.1. Apparatus and equipment

All Spectrophotometric determinations were carried out using Genesys 10S UV – vis Spectrophotometer (Thermo Fisher Scientific Inc., Madison WI, USA). Chemical reagents were weighed using a precision (0.0001 g) balance, (Mettler –Toledo International Inc., Columbus, OH, USA). The accuracy of the balance was checked with standard mass references. Other analytical probes were also used - Hach Sension 3 pH meter (Hach Company, Loveland, Colo. USA). The pH meter was standardized each time before use; LCD portable digital multi-stem thermometer with external probe (Model – ST -9269); A pocket-size conductivity meter (Hanna Instruments, Italy); Hach Sension + DO 6 (Crison Instruments, S.A. Barcelona, Spain).

### 2.2.2. Sampling and sampling procedure

The water samples were collected according to standard procedures (Mendham *et al.* 2004). All items for collecting and storing samples and reagents were first washed with distilled deionised water (DDW), soaked overnight in 10% (v/v) nitric acid and then rinsed exhaustively with DDW. The washed items were dried and stored in zip locked polyethylene bags (Pistón *et al.* 2012). Twelve groundwater samples (six samples per area) were collected twice per month between March and July 2013. Water samples were filtered (except for samples for the determination of analytes other than As(V)) and collected into these precleaned wide mouthed containers (*ca.* 1 litre) with cap. The containers were completely filled with water and capped to prevent spillage. Exposure of the samples to air was minimized during the filtration to reduce the possibility of oxidation (Bednar *et al.* 2004). Tests on each sample were carried out upon return to the laboratory, between one to six hours of collection. Whereupon not possible to meet the period of analysis, there was a re-sampling. pH, temperature, dissolved oxygen; conductivity and turbidity were carried out *in-situ* at the sampling sites using probes.

### 2.2.3. Sample description

The description of the samples and the names of the sample locations are presented in Table 1. The names of the locations are as verified by the locals who assisted in getting through to the sampling location.

**Table 1.** The description of the samples according each local government area

Sample	Location	Description
EN 1	Ezza North	Hand-pumped borehole at Alozie village
EN 2		Hand-pumped borehole at Ogbaga village
EN 3		Hand-pumped borehole at Onunwafor village
EN 4		Hand-pumped borehole at Ogueru village
EN 5		Hand-dug well water at Ogueru village
EN 6		Hand-dug well water at Alozie village
ES 1	Ezza South	Hand-dug well water at Eke Imoha Onueke
ES 2		Hand-pumped borehole at Eke Imoha Onueke
ES 3		Hand-dug well water at Nsokkara Achara Ukwu
ES 4		Hand-pumped borehole at Nsokkara Achara Ukwu
ES 5		Hand-dug well water at Ezama Amaolenya village
ES 6		Hand-pumped borehole at Ezama Amaolenya village

### 2.2.4. Determination of As(V)

Several methods have been optimised for the determination of total and speciated forms of arsenic in water (Pistón *et al.* 2012; Villa-Lojo *et al.* 2002; Bednara *et al.* 2004). This study adopted the method of Nyamah and Torgbor (1986). This is because the technique is relatively simple, affordable, easily available and had proven to be sensitive. The technique is based on the quantitative reaction of arsenate with iodide, releasing an equivalent amount of iodine in the presence of sulphuric acid. The liberated iodine is then extracted immediately with carbon tetrachloride and the absorbance measured spectrophotometrically at 515 nm (Nyamah and Torgbor, 1986).

### 2.2.5. Determination of Physicochemical parameters (total hardness and alkalinity)

The total hardness (TH) and total alkalinity (TA) were determined according to the guidelines of American Public Health Association (APHA), American Water Works Association (AWWA) and Water Environment Federation (WEF), (2012).

### 2.2.6. Determination of Phosphate

The phosphate content of the samples were analysed as described elsewhere (Omaka, 2007).

### 2.2.7. Determination of Nitrate

Nitrate content of the samples were determined as described in Jenkins and Medsken (1964).

### 2.2.8. Determination of Sulfate

The method for the determination of sulfate was based on the reaction of sulfate with barium chloride as described in APHA, AWWA and WEF, (2012).

### 2.2.9. Determination of Chloride

The chloride content of the samples was determined as described in APHA, AWWA and WEF (2012).

## 3. Statistical analysis

The data generated in this study were computed using Microsoft Excel Spreadsheet 2007 (Data analysis ToolPak). The descriptive statistics and correlation analysis were computed using Microsoft Excel

Spreadsheet 2007. The factor analysis model was performed using Paleontological Statistics (PAST) software Package for Education and Data Analysis, version 2.17c (2013).

#### 4. Results and Discussion

The results of the chemical contaminants analysed in this study are presented in Table 2. The results were categorized according to each local government area for easy understanding. The mean values ( $n = 6$ ) were compared with Water Quality Standards (WQS) set by World Health Organisation (WHO, 2011), Standard Organisation of Nigeria (SON, 2007) and National Agency for Food, Drug Administration and Control (NAFDAC, 2007) in Nigeria. The skewness and kurtosis of each contaminant is also presented. The Skewness characterizes the degree of asymmetry of a distribution around its mean. Positive skewness indicates a distribution with an asymmetric tail extending toward more positive values. Negative skewness indicates a distribution with an asymmetric tail extending toward more negative values. The Kurtosis characterizes the relative peakedness or flatness of a distribution compared with the normal distribution. Positive kurtosis indicates a relatively peaked distribution. Negative kurtosis indicates a relatively flat distribution. The mean value ( $n = 10$ ) of each contaminant for each sample is represented graphically in Figures 3 and 4. Generally from the results, within period of this study, no great seasonal variations of parameters from the sampled groundwater were observed. Rather, a temporal trend of the parameters was observed.

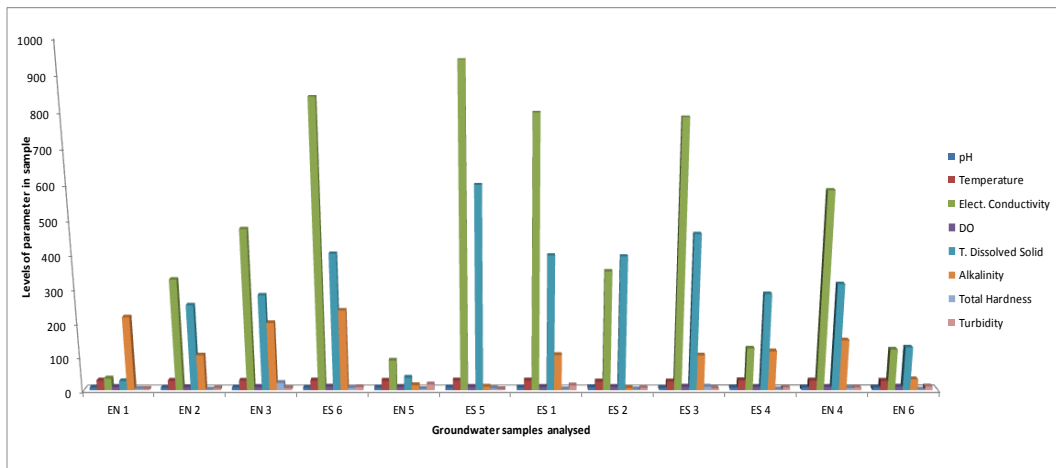
##### 4.1. Physicochemical parameters

The pH of the samples was alkaline, and was within the upper limits of the prescribed standards except for the sample, ES 5, which was slightly above the limit with 0.1 unit (pH 8.6). However, the results of the pH showed that the water samples were not influenced by treatment breakdowns (for the boreholes) or other accidental spills (for the hand-dug wells) which affect the pH of groundwater (Sundaram *et al.* 2009). The temperature range of the water samples could be described as ambient since they are slightly above the normal room temperature (25 °C). The ambient temperature of the samples will contribute little impact on the levels of inorganic constituents and chemical contaminants. The electrical conductivities of ES 1, ES 6 and ES 5 were very high (800, 843 and 943  $\mu\text{S cm}^{-1}$  respectively,  $n = 10$ ) which are consistent with the high total dissolved solids (TDS) recorded (398, 403 and 599  $\text{mg l}^{-1}$  respectively). According to WHO (2011) the palatability of water with a total dissolved solids (TDS) level of less than about 600  $\text{mg l}^{-1}$  is generally considered to be good and drinking-water becomes significantly and increasingly unpalatable at TDS levels greater than 1000  $\text{mg l}^{-1}$ . In that regards, the levels of TDS recorded in the water samples are not considered hazardous to the villagers. Samples EN 1, EN 3 and EN 6 gave high mean levels ( $n = 10$ ) of alkalinity (217.7  $\text{mg l}^{-1}$ , 200.7  $\text{mg l}^{-1}$  and 237.7  $\text{mg l}^{-1}$  respectively). This could have resulted from the dissolved bicarbonates (especially magnesium bicarbonates) abundant in the areas. Water hardness of the samples were found to be relatively high especially for sample EN 3 (21.6  $\text{mg l}^{-1} \text{CaCO}_3$ ), ES 3 (10.4  $\text{mg l}^{-1} \text{CaCO}_3$ ), ES 6 (6.5  $\text{mg l}^{-1} \text{CaCO}_3$ ) and EN 4 (6.2  $\text{mg l}^{-1} \text{CaCO}_3$ ). Though there is no notable health implications of hardness of water (WHO, 2011), the levels of water hardness recorded were far below the prescribed standard. Generally, samples from the hand-dug wells were found to have high levels of turbidity than samples from boreholes. This is expected since they are poorly constructed (hand-dug), open and non-cemented. This resulted in high incidences of particle and dust deposition and seepages from nearby potholes or drainages. This may be the possible explanation to high turbidity levels recorded in EN 5 (17 NTU) as there were lots of mini-potholes around the well occasioned by rainfall, flooding and erosions. Comparing all the samples on the basis of the levels of physicochemical parameters recorded, ES 6 seemed to be highly polluted, with almost high levels of all the parameters. This could be possibly linked to the effects agricultural and commercial activities close to the site.

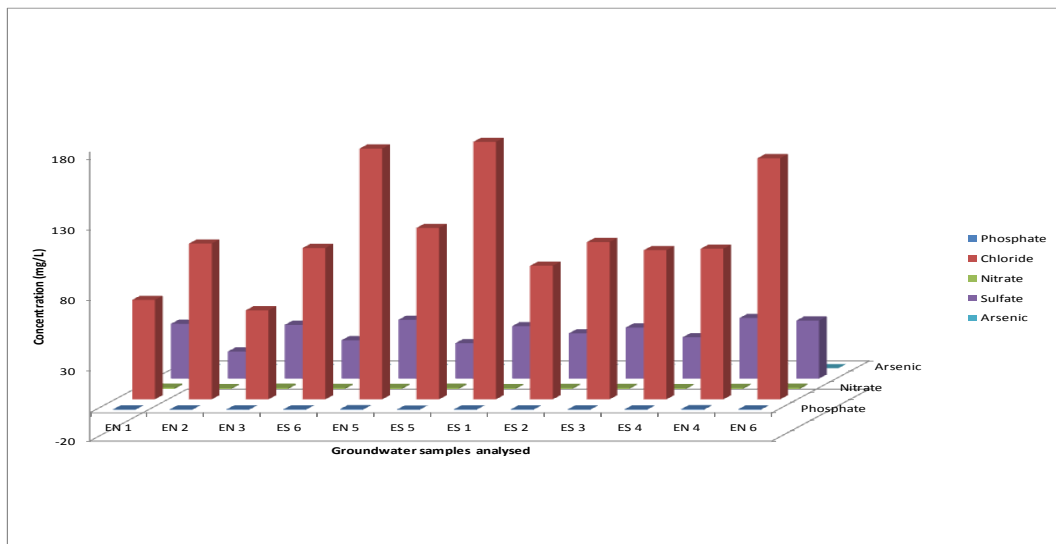
**Table 2.** The chemical contaminants analysed in water samples collected from the two local government areas ( $n = 6$ )

Location	Analyte	Unit	Concentration			Skewness	Kurtosis	WQS		
			Range	Mean	S. variance			WHO	NAFDAC	SON
Ezza South	pH	-	7.30 – 8.60	7.9	0.227	0.343	-0.218	6.5 – 8.5	-	6.5 – 8.5
	Temperature	°C	26.20 – 29.80	28.1	2.746	-0.781	-1.620	-	-	Ambient
	Elect. Conductivity	$\mu\text{S cm}^{-1}$	125.0 – 943.0	641.7	105675.867	-1.045	-0.655	-	-	1000.0
	Dissolved Oxygen	$\text{mg l}^{-1}$	9.40 – 10.20	9.9	0.094	-0.692	-0.632	-	-	-
	T. Dissolved Solid	$\text{mg l}^{-1}$	286.0 – 599.0	423.5	10584.300	0.773	1.930	600	-	-
	Alkalinity	$\text{mg l}^{-1}$	6.70 – 237.70	97.0	7184.267	0.695	0.719	-	100.0	-
	T. Hardness	$\text{mg l}^{-1}$ $\text{CaCO}_3$	1.80 – 6.50	4.6	11.652	1.101	0.430	-	-	150
	Turbidity	NTU	3.00 – 14.00	7.7	14.267	0.755	1.100	5	-	5
	Phosphate	$\text{mg l}^{-1}$	0.130 – 0.180	0.162	0.000	-0.839	-0.059	-	-	-
	Chloride	$\text{mg l}^{-1}$	105.8 – 182.6	120.623	997.603	2.041	4.503	250.0	-	-
	Nitrate	$\text{mg l}^{-1}$	0.59 – 0.85	0.718	0.009	-0.222	-0.874	5 – 50	-	-
Sulfate	$\text{mg l}^{-1}$	25.09 – 37.17	31.182	23.753	0.122	-1.815	-	-	100	
Arsenic(V)	$\text{mg l}^{-1}$	0.006 – 0.011	0.008	0.000	0.962	-1.834	0.010	-	0.010	
Ezza North	pH	-	7.60 – 8.10	7.9	0.035	-1.281	1.853	6.5 – 8.5	-	6.5 – 8.5
	Temperature	°C	28.10 – 29.30	28.7	0.234	0.296	-1.707	-	-	Ambient
	Elect. Conductivity	$\mu\text{S cm}^{-1}$	35.0 – 584.0	272.0	272.0	0.420	-1.909	-	-	1000.0
	Dissolved Oxygen	$\text{mg l}^{-1}$	9.55 – 10.20	9.7	0.134	-0.543	1.276	-	-	-
	T. Dissolved Solid	$\text{mg l}^{-1}$	27.0 – 315.0	173.7	16055.86	-0.178	-2.469	600	-	-
	Alkalinity	$\text{mg l}^{-1}$	14.7 – 217.7	120.0	7176.667	-0.176	-1.963	-	100.0	-
	T. Hardness	$\text{mg l}^{-1}$ $\text{CaCO}_3$	1.2 – 21.60	6.2	60.387	2.186	4.915	-	-	150
	Turbidity	NTU	4.00 – 17.00	8.5	23.500	1.264	1.176	5	-	5
	Phosphate	$\text{mg l}^{-1}$	0.14 – 0.42	0.253	0.016	0.800	-1.911	-	-	-
	Chloride	$\text{mg l}^{-1}$	63.16 – 177.9	116.665	2367.889	0.360	-1.808	250.0	-	-
	Nitrate	$\text{mg l}^{-1}$	0.64 – 0.89	0.792	0.009	-0.692	-0.430	5 – 50	-	-
Sulfate	$\text{mg l}^{-1}$	19.21 – 42.94	36.990	79.109	-2.229	5.157	-	-	100	
Arsenic(V)	$\text{mg l}^{-1}$	0.002 – 0.011	0.005	0.000	1.360	2.149	0.010	-	0.010	

WQS = water quality standards according to World Health Organisation (WHO, 2011), Standard Organisation of Nigeria (SON, 2007) and National Agency for Food, Drug Administration and Control (NAFDAC, 2007), Nigeria as reported in Duruibe *et al.* (2007)



**Figure 3.** The mean values ( $n = 10$ ) of physicochemical contaminants in the groundwater samples in the two areas



**Figure 4.** The mean values ( $n = 10$ ) of targeted and other chemical contaminants in the groundwater samples in the two areas

#### 4.2. Phosphate and Nitrate

The results obtained for phosphate and nitrate were within the WQS prescribed limits. The study of the levels of phosphate and nitrate concentrations in the samples was important for various reasons. Phosphate and nitrate enrichment of waters contributes to ecological impacts (Prior and Jones, 2002) and are notable characteristic pollutants for eutrophication of natural waters (Zanin *et al.*, 1998; Withers and Lord, 2002; Halliwell *et al.*, 1996). Also, high concentration of nitrate in drinking water sources can be fatal to humans and animals (Monteiro *et al.*, 2003; Zatar *et al.*, 1999), while elevated concentration of phosphorus results in fouling of natural water and production of toxic cyanobacteria (Omaka, 2007). Finally, the study areas are rural communities where domestic agricultural practices are predominant (although Ezza North is noted for quarry mining). It is expected that agricultural activities, such as the use of phosphate and urea fertilizers, could contribute significantly to the concentrations of the nutrients in the samples analyzed. High levels of nutrient contamination of water sources are best managed by protecting the source water from contamination. This is because they are difficult to remove, although disinfection will oxidize nitrite (the more toxic form) to nitrate (WHO, 2011). The relatively high mean levels ( $n = 10$ ) of phosphate in EN 4 and EN 5 (0.42 and 0.41 mg l<sup>-1</sup> respectively) is likely from agricultural

activities which are also carried in the area. This could also be true of EN 1 and EN 6 (0.88 mg l<sup>-1</sup> and 0.89 mg l<sup>-1</sup> respectively). Generally, with high levels of phosphate and nitrate in ES 4, the sample could be considered as the most polluted even though the levels are within the limits.

#### 4.3. Sulfate and chloride

From the graphical representation in Figure 4, the results of sulfate and chloride are highly noticeable because they show high mean concentrations especially the chloride. Compared with the WQS, they are below the prescribed limits. However, the presence of sulfate in drinking-water can cause noticeable taste, and very high levels might cause a laxative effect in unaccustomed consumers. It is true that WHO has no health-based guideline value derived for sulfate, the organisation believes that taste impairment varies with the nature of the associated cation and that taste thresholds have been found to range from 250 mg l<sup>-1</sup> for sodium sulfate to 1000 mg l<sup>-1</sup> for calcium sulfate (WHO, 2011). The levels of chloride found in the water samples analysed in this study could have originated from natural sources (geochemistry).

**Table 3.** The values of correlation matrix for the analytes in Ezza North

Analyte	pH	Temp.	EC.	DO	TDS	Alk.	TH	Turb.	PO <sub>4</sub> <sup>3-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	As(V)
pH	1.00												
Temp.	0.01	1.00											
EC.	-0.40	-0.15	1.00										
DO	0.04	-0.37	0.14	1.00									
TDS	-0.21	-0.27	<b>0.88</b>	0.05	1.00								
Alk.	-0.51	0.37	0.10	0.04	-0.13	1.00							
TH	-0.24	-0.09	0.30	0.20	0.18	0.47	1.00						
Turb.	0.31	0.17	-0.21	0.38	-0.38	-0.26	-0.29	1.00					
PO <sub>4</sub> <sup>3-</sup>	0.39	0.24	0.20	0.25	0.01	-0.49	-0.20	<b>0.74</b>	1.00				
Cl <sup>-</sup>	0.43	-0.50	-0.41	0.41	-0.38	-0.98	-0.61	<b>0.87</b>	<b>0.55</b>	1.00			
NO <sub>3</sub> <sup>-</sup>	<b>0.64</b>	0.44	-0.27	<b>0.72</b>	-0.31	0.29	0.20	-0.10	-0.24	-0.15	1.00		
SO <sub>4</sub> <sup>2-</sup>	<b>0.87</b>	<b>0.58</b>	-0.08	<b>0.80</b>	-0.28	-0.04	0.16	0.46	<b>0.51</b>	0.19	<b>0.69</b>	1.00	
As(V)	0.32	0.47	-0.72	0.19	-0.80	0.22	-0.31	-0.05	-0.18	-0.08	<b>0.64</b>	0.43	1.00

Values considered significant are in bold ( $\geq 0.5$ ). Negative significant values show inverse correlation.

Temp. = Temperature, EC. = Electrical Conductivity, DO = Dissolved Oxygen, TDS = Total Dissolved Solid, Alk = Alkalinity, TH = Total Hardness, Turb. = Turbidity

#### 4.4. As(V)

Arsenic is found widely in Earth's crust in oxidation states of -3, 0, +3 and +5, often as sulfides or metal arsenides or arsenates. Irrespective of the specie, the concentration in natural waters is usually less than 1 – 2 µg l<sup>-1</sup>, but could be significantly elevated in the presence of sulfide mineral deposits and sedimentary deposits derived from volcanic rocks (WHO, 2011). The results of the 12 groundwater samples of this study showed varied concentrations, which are believed to be strongly related to natural geochemistry, rather than anthropogenesis. This is because of the relatively low concentrations observed in the samples. The concentrations of arsenic(V) in the samples from Ezza South area gave mean values ( $n = 10$ ) of approximately 0.006 mg l<sup>-1</sup>, except for ES 1 and ES 4 which had mean values of 0.010 and 0.011 mg l<sup>-1</sup> respectively. These results strongly suggest similar sources of enrichments or contamination. ES 1 is a hand-dug well water sample and this could have contributed to the mean value. The samples from Ezza North had relatively lower mean concentrations (< 0.007 mg l<sup>-1</sup>), except for EN 1 (0.011 mg l<sup>-1</sup>). The values do not reflect effects of contamination from quarry mining activities in the area contrary to expectations. Generally, environmental factors such as redox potentials or presence of Fe-Mn oxyhydroxides, particularly Mn oxides, could have affected the levels (enrichment) of arsenic(V) in the water samples. This is because dissolved heavy metals adsorb strongly to Mn oxides due to its large specific surface area, and Mn is widespread in the environment (Heal, 2001). These factors were not investigated in this study. However, there is possibility of bio-accumulation of As(V) in human and other animal consumers of the water samples since As(V) has not been demonstrated to be highly essential to humans. Acute toxicity of



arsenic compounds in humans is predominantly a function of their rate of removal from the body (Steiner-Asiedu, *et al.* 2010).

**Table 4.** The values of correlation matrix for the analytes in Ezza South

Analyte	pH	Temp.	EC.	DO	TDS	Alk.	TH	Turb.	PO <sub>4</sub> <sup>3-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	As(V)
pH	1.00												
Temp.	-0.03	1.00											
EC.	-0.46	-0.05	1.00										
DO	-0.32	-0.55	0.08	1.00									
TDS	-0.15	-0.19	<b>0.77</b>	-0.34	1.00								
Alk.	-0.68	0.32	0.15	<b>0.56</b>	-0.42	1.00							
TH	-0.84	-0.47	<b>0.57</b>	0.45	0.42	0.33	1.00						
Turb.	0.19	0.35	-0.08	0.30	-0.58	0.43	-0.43	1.00					
PO <sub>4</sub> <sup>3-</sup>	0.27	-0.10	-0.34	<b>0.69</b>	-0.69	0.44	-0.32	<b>0.66</b>	1.00				
Cl <sup>-</sup>	0.08	0.35	0.41	-0.15	0.08	0.04	-0.20	<b>0.68</b>	-0.03	1.00			
NO <sub>3</sub> <sup>-</sup>	-0.19	-0.36	<b>0.62</b>	-0.06	<b>0.86</b>	-0.26	0.49	-0.73	-0.42	-0.36	1.00		
SO <sub>4</sub> <sup>2-</sup>	0.07	-0.47	-0.03	0.46	-0.29	-0.03	0.11	<b>0.50</b>	0.28	0.49	-0.48	1.00	
As(V)	0.19	<b>0.61</b>	-0.39	-0.24	-0.62	0.18	-0.56	<b>0.73</b>	0.17	<b>0.60</b>	-0.92	0.35	1.00

Values considered significant are in bold ( $\geq 0.5$ ). Negative significant values show inverse correlation

Temp. = Temperature, EC. = Electrical Conductivity, DO = Dissolved Oxygen, TDS = Total Dissolved Solid, Alk = Alkalinity, TH = Total Hardness, Turb. = Turbidity

#### 4.5. Correlation analysis

Correlation analysis is used to calculate correlation coefficient between two measurement variables when measurements on each variable are observed for each of  $n$  subjects. Correlation between all the analytes was carried out by using Pearson's correlation matrix. Tables 3 and 4 show the correlation coefficients between the analytes in the study areas. Based on the Pearson's correlation, there is significant and positive correlation (for values  $\geq 0.5$ ) between the two variables marked in bold. This implies that there is relationship between the analytes in each case.

**Table 5.** Factor Analysis numbers (Varimax rotation) of various analytes in Ezza North

Analyte	Factor 1	Factor 2	Factor 3	Factor 4
pH	<b>0.80772</b>	0.55429	-0.17774	0.082885
Temp.	<b>0.79765</b>	0.57227	-0.16722	0.076742
EC.	0.42266	<b>0.88063</b>	-0.1792	-0.11524
DO	<b>0.80916</b>	0.55109	-0.18236	0.086713
TDS	0.45715	<b>0.87732</b>	-0.13662	0.048147
Alk.	0.33196	<b>0.87313</b>	-0.35642	-0.0017481
TH	0.2234	<b>0.62586</b>	-0.74698	-0.013251
Turb.	<b>0.95973</b>	0.20451	-0.16748	-0.069747
PO <sub>4</sub> <sup>3-</sup>	<b>0.86241</b>	0.42647	-0.073672	-0.26044
Cl <sup>-</sup>	<b>0.94675</b>	0.30671	-0.035111	0.088891
NO <sub>3</sub> <sup>-</sup>	<b>0.80337</b>	0.54554	-0.21481	0.09574
SO <sub>4</sub> <sup>2-</sup>	<b>0.83549</b>	0.47991	-0.2468	-0.049982
As(V)	<b>0.93962</b>	0.28254	-0.16654	0.0044065

Values of factors that had strong positive loading on the analyte are in bold ( $\geq 0.6$ ).

Temp. = Temperature, EC. = Electrical Conductivity, DO = Dissolved Oxygen, TDS = Total Dissolved Solid, Alk = Alkalinity, TH = Total Hardness, Turb. = Turbidity

#### 4.6. Factor analysis model

Factor analysis is a statistical method used to identify "factors" that explain a variety of results on different tests. Through the factor analysis, assumptions are made that underlying causal models exist in results on different tests. This assumption is based on the fact that parameters with loadings whose absolute value is more than 0.6 are considered significant (Selvakumar *et al.* 2014). In this study, the spatial distributions

of different chemical analytes were related to different possible sources (factors), which have different chemical signatures. The results showed that the analytes in each of the study area was affected by four factors. However, two factors (1 and 2 for Ezza North, 1 and 3 for Ezza South) have strong positive loading on some of the parameter and were considered significant (values are  $\geq 0.6$ ).

Factor 1 had strong positive loadings on pH, temperature, dissolved oxygen, total dissolved solid, turbidity,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and As(V) in the two study areas. The positive loadings suggested that results could have been influenced by natural causes, possibly from the soil's geochemistry. Factor 2 (for Ezza North) and factor 3 (for Ezza South) had strong positive loadings on electrical conductivity, alkalinity and total hardness. The positive loadings suggested that results could have resulted from anthropogenic causes, possibly from the agricultural, commercial and mining activities. Factors 2 and 4 (for Ezza North) and factors 2 and 4 (for Ezza South) had little loadings on the analytes.

**Table 6.** Factor Analysis numbers (Varimax rotation) of various analytes in Ezza South

Analyte	Factor 1	Factor 2	Factor 3	Factor 4
pH	<b>0.83676</b>	-0.30859	0.45168	0.0155
Temp.	<b>0.80929</b>	-0.35955	0.46144	0.033085
EC.	0.49623	-0.3002	<b>0.79968</b>	0.15532
DO	<b>0.79828</b>	-0.35852	0.48347	-0.01016
TDS	<b>0.73352</b>	-0.21394	<b>0.63886</b>	0.087677
Alk.	0.35661	-0.87093	0.33641	0.0032852
TH	0.39978	-0.40232	<b>0.79729</b>	-0.20651
Turb.	<b>0.7769</b>	-0.56298	0.26666	-0.00071273
$\text{PO}_4^{3-}$	<b>0.80943</b>	-0.4007	0.42153	0.0016363
$\text{Cl}^-$	<b>0.78114</b>	-0.32851	0.52742	0.019845
$\text{NO}_3^-$	<b>0.77146</b>	-0.2989	0.55841	0.05542
$\text{SO}_4^{2-}$	<b>0.79831</b>	-0.33064	0.48739	-0.11677
As(V)	<b>0.8553</b>	-0.37922	0.31815	-0.052678

Values of factors that had strong positive loading on the analyte are in bold ( $\geq 0.6$ ).

Temp. = Temperature, EC. = Electrical Conductivity, DO = Dissolved Oxygen, TDS = Total Dissolved Solid, Alk = Alkalinity, TH = Total Hardness, Turb. = Turbidity

#### 4.7. Comparison with other Reports of Groundwater Studies

A comparison of the observed mean concentrations of chemical contaminants in this study with those reported in previous studies conducted in an area of Ghana (Tarkwa area) shows that they were of the same magnitude with their turbidity (10 – 34 NTU), TDS (40 – 654  $\text{mg l}^{-1}$ ) and conductivity (68.9 – 105  $\mu\text{S cm}^{-1}$ ) (Armah *et al.* 2010). However, for the As, their mean values ranged from 0.000 – 0.004  $\text{mg l}^{-1}$ . With regards to As(V), mean values of 0.0036 – 0.0252  $\text{mg l}^{-1}$  were found in Agyapesuwa, Agona and Bumafua (Ghana) (Nyamah and Torgbor, 1986). As concentrations greater than 10  $\mu\text{g l}^{-1}$  was reportedly found in privately owned drinking wells in New England (Ayotte *et al.* 2003) and a review published in 2012 of 14 Latin American countries showed As concentrations greater than 10  $\mu\text{g l}^{-1}$  for a century (Bundschuh *et al.* 2012).

## 5. Conclusion

This study has shown that the quality of the groundwater samples in rural areas of Ebonyi State, South-eastern Nigeria are influenced mainly by soil's geochemistry and slightly by commercial or agricultural activities. There was no evidence that the proximity of sampled points to the quarry mine-pits in Ezza North influenced the levels of the chemical contaminants analysed in that area. The results of the factor analysis suggested that most of the variations are explained by the set of natural causes (soil's geochemistry) and anthropogenic causes. Adequate monitoring of As(V), and other potential toxic contaminants in groundwater samples is advocated as this will help local authorities set new guidelines for various contaminants that affect water quality.

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