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Metal Survey of Surface Water in Parts of Odukpani, South-Eastern Nigeria

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Abstract: *This study was aimed at assessing the concentration of some major elements (Na, Mg, K, Ca and Fe) and trace elements (Cu, Co, Pb and Zn) in surface water in Odukpani, South Eastern Nigeria; a developing area which has its habitants in direct contact with the stream channels and surface waters. The results show the mean pH level in surface water, in comparison to the World Health Organization and the Nigerian Industrial Standard values, alongside the total dissolved solids and the concentration of these elements in specific locations across the area. The concentrations of these elements in surface water can impose serious damage to the organisms in the streams and man, either through the food chain or direct contact with the water, if they exceed the World Health Organization's standard ph levels. Thus, a detailed study is recommended to identify the exact source of metal contamination, in order to ascertain the occurrence of profitable deposits of Ca, Fe, Cu, Pb and Zn, also, measures should be put into place in order to monitor and mitigate the deleterious effects of these above-limit metals in the environment, especially lead which could lead to very serious health challenges to the inhabitants of the area.*

Keywords: *Atomic Emission Spectrometer, Cross River, Lead, Metal Survey, Nigeria, Odukpani, South-Eastern Nigeria*

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I. Introduction

Metal surveys can be carried out using water samples, soil samples, stream sediment samples as well as plants to estimate the distribution and concentration of selected metals (elements) in an area. For the purpose of this study, nine (9) surface water samples from streams in Odukpani, South Eastern Nigeria were analyzed for selected elements which include five (5) major elements (Na, Mg, K, Ca and Fe) and four (4) trace elements (Cu, Co, Pb and Zn) in order to determine their concentrations at different locations across the area (Table 1, Fig. 3, Fig. 4, Fig. 5), and compare these concentrations to the World health Organization and the Nigerian Industrial Standard water quality (Table 2).

II. The Study Area

The study area (Odukpani) is the capital of Odukpani Local Government Area in Cross River State, Nigeria (Fig. 1). It falls under the Calabar Flank located in the South Eastern Part of Nigeria, and lies between longitudes $8^o15´00´´$E and $8^o25´00´´$E and latitudes $5^o055´00´´$N and $5^o15´00´´$N, and is approximately 14 km^2 (Fig. 2). According to Ukpong, & Ekhalialu (2015), structurally, the Calabar Flank consists of basements horsts and grabens that aligned in a NW-SE direction like other South Atlantic marginal basin in West Africa. Sedimentation started in the Calabar Flank with the deposition of fluvio-deltaic clastics (the Awi Sandstone) of probably Aptain age on the Precambrian crystalline basement complex, the Oban Massif. This was followed by the first marine transgression in the Mid Albian which accounts for the deposition of the Mfamosing Limestone, particularly on the horst and relatively stable platform areas and their flanks. The Mfamosing Limestone is overlain by the thick sequence of black to grey shale unit, the Ekenkpon Formation. The formation is characterized by minor intercalation of marls; calcerous mudstone and oysters beds. This shale unit was deposited during the late Cenomarian-Turonian times. The Ekenkpon Shale is overlain by a thick marl unit; the New Netim Marl. The study area has a low relief, and the drainage system comprises streams which flow in a dendritic pattern into the Calabar River. The vegetation is that of tropical rainforest (Iloeje, 2001) and is characterized by a tropical climate with two distinct seasons which are the wet and dry season. The wet season starts from May to October while the dry season last from November to April. The average monthly temperature in the area ranges from 29-40^{o}C. Mean annual rainfall of about 2,300mm has been reported for the area, with annual mean daily relative humidity and exploration of 86% and 3.85nm/dry respectively (CRBPA, 2008).

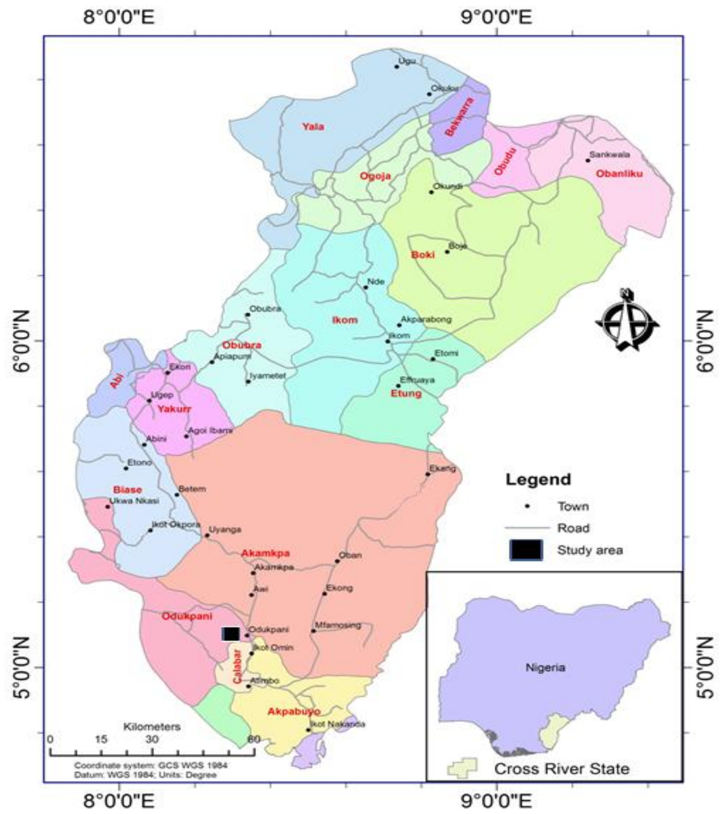

Fig. 1: Map of Cross River State showing the Study Area

III. Literature Review

According to Nganje *et al.* (2015), most of the rural population in South Eastern parts of Nigeria depend on rainfall, ponds, streams, rivers, hand dug wells and boreholes for their daily water needs. In several cases, this water is not treated before use resulting in diseases such as cholera, typhoid fever, Guinea worm infection, bilharzias etc. It has been reported by some workers (e.g. Subba, 2006) that the quality and quantity of water is important for the sustainable development of an area. Thus, understanding the quality and quantity of water resources of a community is important as it is the main factor determining its suitability for domestic and agricultural uses (Subramani *et al.* 2005; Kumar *et al.* 2007; Ketata *et al.* 2011). Metals are common pollutants which are distributed in streams. They may occur due to industrial, agricultural constructional and commercial activities. Most heavy metals in coastal waters are leached to rivers by industrial, urban and agricultural. Some of these (e.g. Cu, Zn, Fe, Co) are essential for living organisms. However, some (e.g. Pb, Cd, Hg) are toxic to living organisms. They impose serious damage to metabolic and structural systems of organisms when present in high concentrations in the environment. Metals such as Zinc and Copper are essential elements for normal metabolism of aquatic organisms in low concentrations. They may have direct effects on organisms by accumulating in their body or indirectly through food web to the next trophic level. One of the most serious consequences of this transfer is biological amplification through the food chain (Koffi *et al.*, 2014). In water, the distribution processes of the metals set off physicochemical interactions and their solubility is principally controlled by pH, concentration, type of metal species, organic ligands among other factors. After being introduced into the aquatic environment via various sources and paths, metals are adsorbed onto inorganic and organic particulates and are incorporated into sediment resulting in elevated levels of heavy metals in bottom sediment physicochemical parameters play an important role to determine the water quality. As water travels through the soil's profile, various water-soluble substances are released into the water. Some also precipitate out of the water into the sediments. The composition and concentration of substances in surface water is a resultant of two factors: the geological structure of the earth's crust, including the intensity with which it is leached, and anthropogenic activity associated with agriculture, industry and public utilities (Orzepowski & Pulikowski, 2008).

IV. Methodology

4.1 Sample Collection: Nine (9) surface water samples were collected at in the study area. The water samples were collected in clear 75cm^3 transparent plastic bottles away from the bank to avoid contamination and labelled properly. Duplicate water samples were collected and stored in polyethylene bottles of same size. The bottles were rinsed thoroughly with water from the sampling location before the water samples were collected.

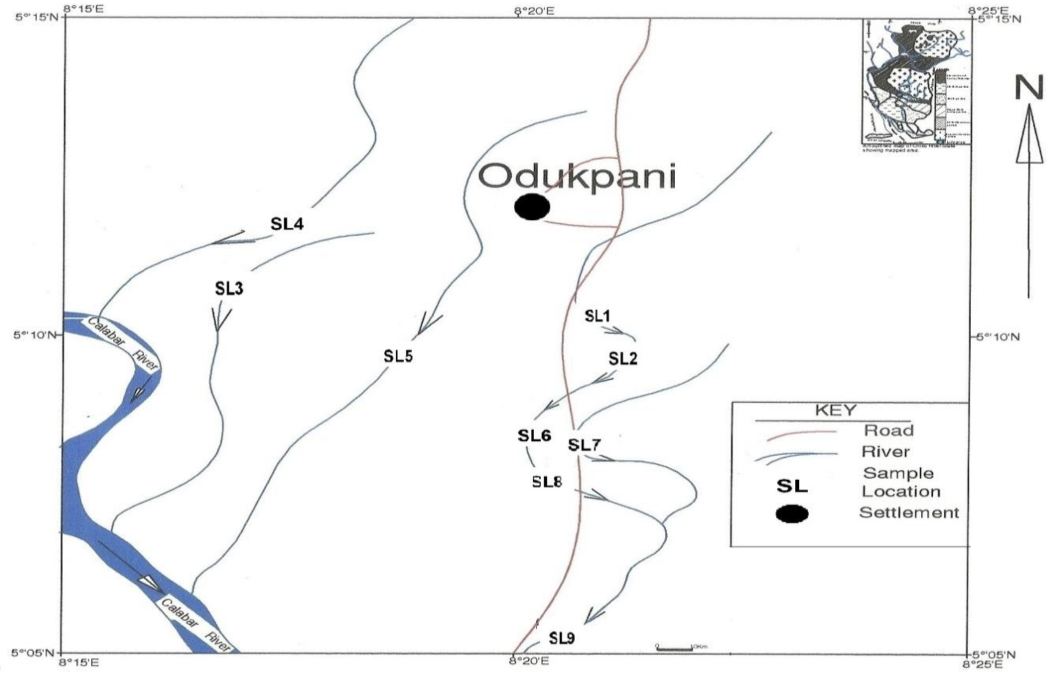

Fig. 2: Map showing the Drainage and Sample Location in the Study Area

4.2 Sample Preparation: The surface water samples involved acidification by adding 2 drops of HNO_3, in order to prevent microbial growth and to cause reaction in the water samples so that each element present can manifest itself or to maintain ions in solution because in acidic water, metal ions remain in solution while in basic water the ions may flocculate out of the solution, thereby influencing the overall concentration analysis of the solution. The samples are then stored under cool conditions prior to analysis.

4.3 Analysis: Major and trace elements in the sediment and water sample extracts were analyzed on a Varium Vista Pro Ax Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) at Acme Laboratory Limited, Vancouver, Canada. The detection limits were based on three times the standard deviation of a reagent blank that was analysed several times. An external standard (SRM-1640) was run in between the samples, and the standard deviation was <10% for elements of interest. The pH of the water samples was measured using a Knick Portatest 630pH metre in combination with Orion type 91-08 combination electrode. The concentration of the Total Dissolved Solids (TDS) was measured by TDS/conductivity meter.

V. Results and Data Presentation

Table 1: Results of Surface Water Analysis in the Study Area

SAMPLE LOCATION	pH	TDS (mg/L)	METALS (mg/L)								
			Na	Mg	K	Ca	Fe	Co	Cu	Pb	Zn
SL1	6.6	426	4.06	2.38	2.00	19.32	0.71	0.003	0.10	0.020	1.78
SL2	7.1	236	2.40	2.76	1.26	3.19	8.86	0.002	0.17	0.015	0.70
SL3	6.8	317	8.10	12.21	2.58	110.80	0.62	0.001	0.01	0.030	1.61
SL4	6.4	604	5.90	21.33	5.54	118.40	1.60	0.005	0.004	0.014	0.13
SL5	6.4	156	2.80	8.90	2.63	9.59	0.60	0.034	0.006	0.030	0.35
SL6	7.2	387	7.54	14.12	6.02	62.08	0.44	0.070	0.02	0.010	0.47
SL7	7.3	331	12.89	48.35	1.56	387.50	25.75	0.200	0.06	0.013	1.93
SL8	7.3	249	9.76	1.95	3.01	10.80	1.75	0.002	0.02	0.026	1.83
SL9	6.5	237	2.06	1.03	1.33	5.80	0.90	0.002	0.003	0.020	0.50

Table 2: Descriptive Statistics of Elements Concentrations in Surface Water. Units = mg/L, except pH (no unit)

PARAMETER	RANGE	MEAN ($\bar{x}$)	STANDARD DEVIATION (SD)	W.H.O (2006) *	N.I.S (2007) **
pH	6.4 – 7.3	6.8	0.384	6.5 – 8.5	6.5 – 8.5
TDS	156 – 604	327	133.207	500	500
Sodium (Na)	2.06 – 12.89	6.168	3.719	200	200
Magnesium (Mg)	1.03 – 48.35	12.559	15.079	50	NA
Potassium (K)	1.26 – 6.02	2.881	1.756	12	NA
Calcium (Ca)	3.19 – 387.50	80.831	123.556	75	NA
Iron (Fe)	0.44 – 25.75	4.581	8.371	0.3	0.3
Cobalt (Co)	0.0001 – 0.070	0.035	0.066	NA	0.01
Copper (Cu)	0.003 – 0.17	0.044	0.057	1	1
Lead (Pb)	0.010 – 0.030	0.021	0.008	0.01	0.01
Zinc (Zn)	0.13 – 1.93	1.033	0.735	3	3

Sources: * World Health Organization Standard (2006), ** Nigerian Industrial Standard (2007), NA = Not Available

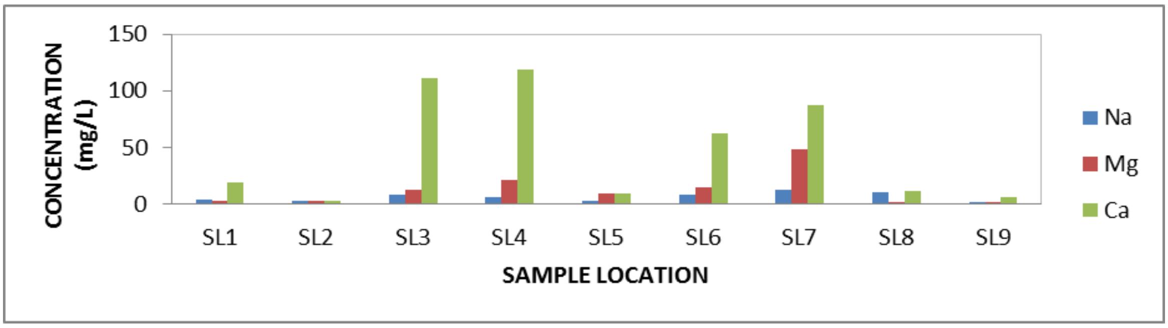

Fig. 3: Concentrations of Elements (Na, Mg and Ca) in Surface Water of the Study Area for Each Location

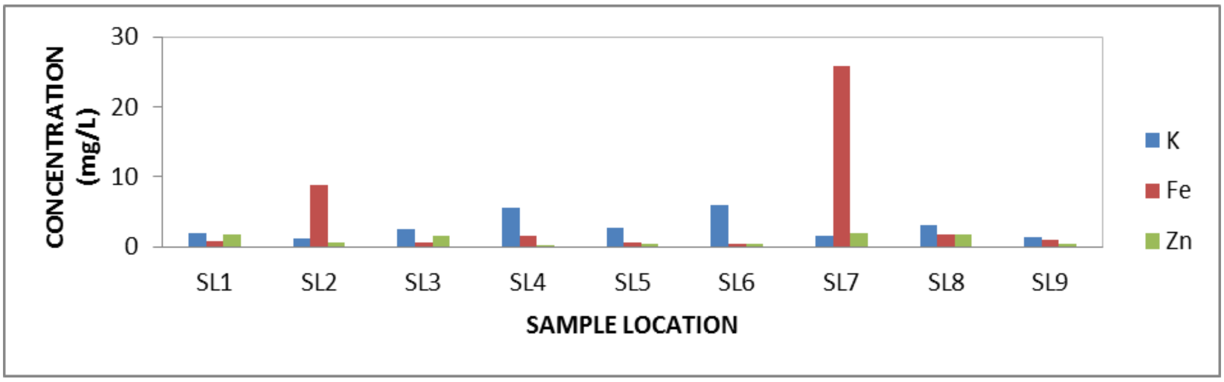

Fig. 4: Concentrations of Elements (K, Fe and Zn) in Surface Water of the Study Area for Each Location

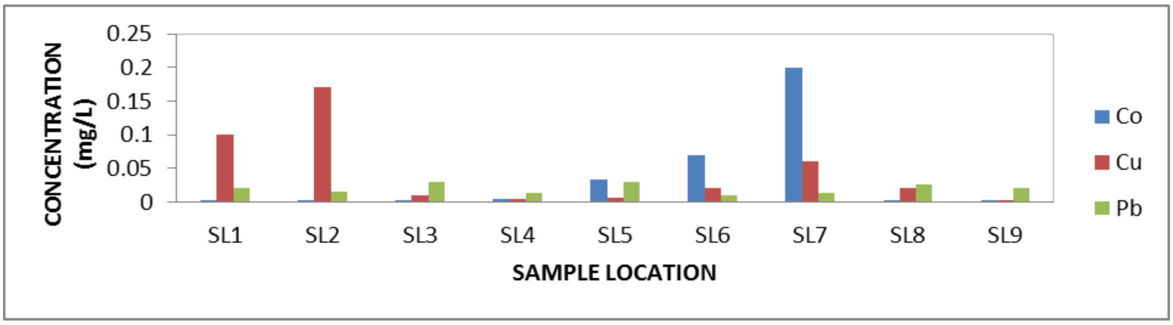

Fig. 5: Concentrations of Elements (Co, Cu and Pb) in Surface Water of the Study Area for Each Location

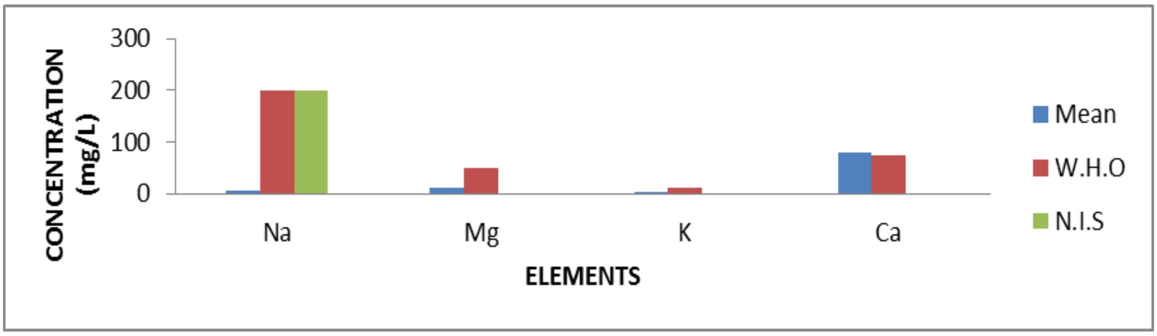

Fig. 6: Comparison of World Health Organization Standard and Nigerian Industrial Standard with Mean Concentrations Values of Elements (Na, Mg, K, and Ca) in Surface Water of the Study Area

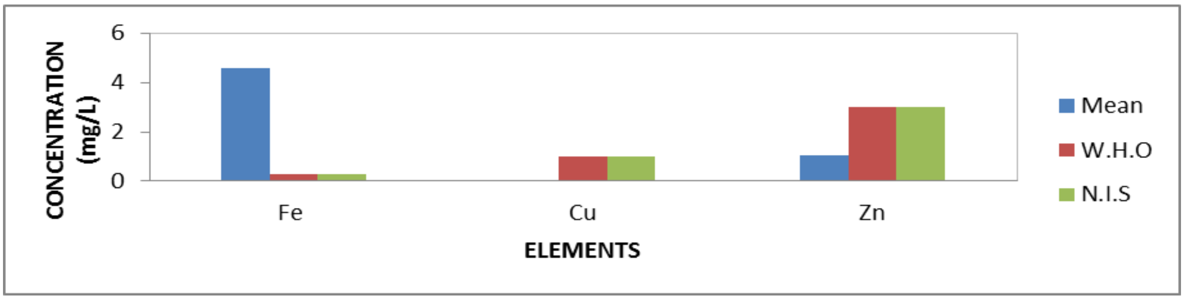

Fig. 7: Comparison of World Health Organization Standard and Nigerian Industrial Standard with Mean Concentration Values of Elements (Fe, Cu and Zn) in Surface Water of the Study Area

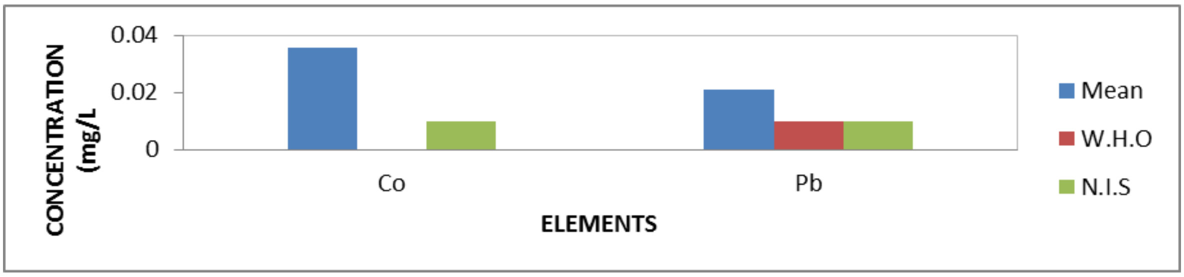

Fig. 8: Comparison of World Health Organization Standard and Nigerian Industrial Standard with Mean Concentration Values of Elements (Co and Pb) in Surface Water of the Study Area

VI. Discussion

The mean pH level falls within the approved standard of the World Health Organization and the Nigerian Industrial Standard, and is approximately neutral, while the mean TDS value is below the World Health Organizations maximum limit (Table 2). The mean concentration values for major elements (Na, Mg and K) are lower than the World Health Organization standard (Fig. 6) while the mean concentration values for the major elements (Fe and Ca) is greater than the World Health Organization standard and the Nigerian Industrial Standard (Fig. 7). The mean concentration values for the trace elements (Cu, Co and Zn) in surface water is lower than the World Health Organization standard and the Nigerian Industrial Standard while the mean concentration value of the trace elements (Pb) is greater than the World Health Organization standard and the Nigerian Industrial Standard (Fig. 8). The high concentrations of Ca, Fe and Pb in surface water could impose serious damage to the organisms in the streams and man through the food chain. Such high concentration suggests that the pollution is from the breakdown of rocks and mineralization (Fe, Cu, Ca, Pb, and Zn), as well as burning fuel (coal or oil), burning of solid waste, industrial processes (primarily from iron and steel industries and lead producers), deposits of lead-containing dust from the atmosphere and mining wastes that have been used for driveways, and roadbeds (Pb). Lead (Pb) in excess pose exhibit toxic effects towards soil biota by affecting key microbial processes and decrease the number and activity of microorganisms and decreases the activities of certain enzymes such as urease, catalase, phosphatase, etc (Karaca *et al.*, 2010). At such high quantity values results in oxidative stress in aquatic organisms resulting in detrimental effects such as death on aquatic flora and fauna, effects is immediately seen in benthic organisms which goes a long way to affecting the food chain as they vital roles in lotic food webs and forming a major link between primary producers and higher trophic levels. It could also result in bio-accumulation in the skin and certain organs of aquatic organism which is then transferred to the top of the food chain (man) and causing both physiological and neurological problems such as dysfunction in the kidney, reproductive system, liver, blood-related diseases, etc. Kazemipour *et al.*, (2008) reports that even at extremely low concentrations, Pb is still highly dangerous to man.

VII. Conclusion

A detailed study is recommended to identify the exact source of metal contamination in order to ascertain the occurrence of profitable deposits of Ca, Fe, Cu, Pb and Zn, also, measures should be put into place to monitor and mitigate the deleterious effects of these above-limit metals in the environment, especially Lead (Pb) which could pose severe health challenges to the inhabitants of the area.

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