Scientific
Research

Evaluation of the Level and Impact of Selected Physiochemical Parameters of Fertilizer Effluent on Obinna River, Adani, Enugu State, Nigeria

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Abstract

This work quantitatively evaluates the level and impact of selected physiochemical properties of fertilizer effluent on the Obinna River of Adani, Enugu State, Nigeria. The fertilizer effluent originated from surrounding farms and flushed into the Obinna River. Water samples were collected from designated points along the river and analysed for physical, chemical and biological properties using standard methods of APHA. Impact of selected key parameters such as nitrate, phosphate, manganese, dissolved oxygen, biochemical oxygen demand and heavy metals (lead, iron and manganese), was studied. The results of the parameters were compared with the World Health Organisation (WHO) permissible standard for freshwater. Measured concentrations of phosphate (5.00, 7.21, 3.92 mg/L), manganese (1.53, 1.18, 1.47 mg/L) and lead (18.9, 21.7, 39.7 ppm) were found to be above the WHO standard while nitrate (0.04, 0.03, 0.03 mg/L) and iron (0.001, 0.001, 0.1 mg/L) were within the standard. The mean concentrations of heavy metals increased in the following order: Fe (0.034) < Mn (1.4) < Pb (26.8) from upstream S_1 to downstream S_3, with manganese and lead being above WHO standard. The results showed a level of significance for the chi-square distribution and correlation coefficients while the analysis of variance (ANOVA) results was conflicting. It could be inferred that the impact of the selected parameters contributed to the pollution of Obinna River.

Keywords

Physiochemical, Heavy Metals, WHO, Pollution, Obinna River

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1. Introduction

A major cause of freshwater scarcity is the application of agricultural chemicals such as chemical fertilizers and pesticides for assured "better" resource harvesting. These chemical fertilizers contain volumes of elements ranging from macro nutrients such as nitrates, phosphates and potassium to secondary plant nutrients and trace elements such as calcium, magnesium, sulphur, boron, manganese, iron, molybdenum and copper. The use of these agricultural chemicals induces pressure on ecosystems and can directly or indirectly, positively or negatively affect the services of a functioning ecosystem. And, as long as the world faces an increase in global, regional and local populations, there will always be some added pressure on the natural resource base—the land, for increased food production. [1] noted that the most common causes of water body impairment are sediments, pathogens, nutrients, metals, dissolved oxygen and other habitat alteration and agricultural practices, which provide the focus of this study.

Agriculture is the major source of nitrate and phosphate pollution of surface water [2]. Agriculture further contributes to a doubling of nitrogen fixation [3] [4] and a tripling of phosphorous usage [4] [5]. Nitrate may arise from the excessive application of fertilizers or from leaching of wastewater or other organic wastes into surface water and ground water [6]. Taiwo *et al.* [2] noted that nutrient enrichment is predominant in most rivers in Nigeria. Increasing the nutrient (phosphorous and nitrate) concentrations in freshwater, can lead to eutrophication in lakes and rivers as a result of a decrease in the amount of oxygen available to aquatic life, killing fish and other aquatic organisms [7].

Furthermore, heavy metals are potential toxic threats to the environment and ecosystem due to their persistence and bio-accumulation in the food chain, water and organisms [2] [8] [9]. Their accumulation above recommended level is undesirable [10] [11]. Such toxic heavy metals include Hg, Pb, As, Cd, Fe, Co, Mn, Cr, etc. [11] [12], though heavy metals like iron, copper, zinc, nickel, and other trace elements are needed for proper functioning of biological systems. Deficiencies of these trace elements may lead to a number of disorders [13] [14].

Freshwater supplies and wastewaters are known to have a high degree of variability in terms of physico-chemical quality, heavy metal concentration and microbial quality [14]. And as part of global efforts to promote sustainable development, two of the commitments of the World Summit on Sustainable Development (WSSD) in 2002 at Johannesburg include 1) by 2020, that chemicals should be used and produced in ways that do not harm human health and the environment 2) halving the proportion of people without access to safe drinking water by 2015.

It was reported that at least 27 per cent of Nigerians depended absolutely on streams, ponds, rivers and rainwater for their drinking water sources [2] [15]. And also, by 2025, Nigeria would be among 48 countries expected to experience water shortage below the United Nations Development Programme (UNDP) threshold to the tone 1000 to 1700 M^3/person/year [16].

In view of the prevailing challenges, this study becomes very imperative. Thus it attempts to assess the effects of leaching of fertilizer effluent into the Obinna River. Key parameters were identified, quantified and compared with World Health Organisation (WHO) standard, in order to evaluate the level of compliance with the standard. Also, statistical analyses of the result were conducted to evaluate the statistical significance of the obtained results.

2. Materials and Methods

2.1. Study Area

The study was carried out on the Obinna River and samples were collected during high stream flow conditions at a temperature of 26˚C.

The Obinna River is surrounded by lush vegetation of thick trees and shrubs along its banks. It is located at Adani, Uzo-Uwani local government area in Enugu state, Nigeria. And being part of the Anambra river system, it lies on 7˚1'0" East of the Greenwich meridian and 6˚45'0" North of the equator.

Located on the left bank of the river is Adarice farmlands of about 900 hectares. Over the years, the river received fertilizer effluent from this farm and by 2006; the river supplied water for domestic and farm needs as well as natural habitat to aquatic flora and fauna. The map (**Figure 1**) on the following page shows Adani where the Obinna River is located

2.2. Sample Characterization and Analysis

2.2.1. Field Study

The study was limited to three sample points S_1, S_2 and S_3 representing 1) upstream: the river before the point of

Figure 1. Location of sampling site. Source: [17].

wastewater discharge, 2) midstream: the river at the point of wastewater discharge and 3) downstream: the river after the point of wastewater discharge.

Precautions were taken to ensure that the samples were representative of the river.

2.2.2. Laboratory Analysis

The characteristics of the water samples (**Table 1**) were determined by standard APHA method [18]. The quantity of heavy metals was determined by Atomic Absorption Spectrophotometry.

2.2.3. Statistical Analysis

1) Determination of the **per cent change** from S_1 to S_2

$$\left[\frac{S_1 - S_2}{S_1}\right] \times 100 \tag{1}$$

S_1 **is the expected concentration;**
S_2 **is the observed concentration.**
2) Determination of **the chi-square** X^2 for the measured samples

$$X^2 = \sum\nolimits_{i=1}^{n} \frac{(O_i - E_i)^2}{E_i} \tag{2}$$

O_i **is the observed concentration;**
E_i **is the expected concentration (WHO standard);**
n **is the number of cases.**
3) Determination of the **extent of a correlation** using the Pearson's linear coefficient *IrI*

$$IrI = \frac{\sum (X - \bar{X})(Y - \bar{Y})}{\sum \sqrt{(X - \bar{X})^2 (Y - \bar{Y})^2}} \tag{3}$$

X **and** Y **are the pairs of observation;**
$\bar{X}$ **and** $\bar{Y}$ **are the mean of pairs of observation.**
4) Determination of the **mean concentration (*S*)** of heavy metals in water samples.

$$S = \frac{S_1 + S_2 + S_n}{n} \tag{4}$$

$$= \frac{1}{n} \sum_{i=1}^{n} X_i \tag{5}$$

S_1, S_2 and S_n are the variates of heavy metals observed;
n is the total number of observations.
5) Determination of difference using **ANOVA** and the **Coefficient of Variation (CV %)**

$$\text{Coefficient of variation} = \frac{\sqrt{\text{variance}}}{\text{Grand mean}} \times 100 \tag{6}$$

3. Results and Discussion

3.1. Nitrate, Phosphate, BOD and DO Concentrations

Sigmund [19] suggests a maximum level of 0.1 mg/L as the expected level of phosphate in surface stream water. FEPA [20] and Adelekan *et al.* [21] prescribed maximum concentrations of DO and BOD of 2.0 mg/L and 30 mg/L respectively for surface water. These levels suggested that the river was highly polluted at the time of the study.

The phosphate concentration showed a higher per cent change with an increase of 44.2 per cent from S_1 to S_2 while nitrate showed a 25 per cent drop in concentration. The recorded increase in phosphate concentration at S_2 may suggest 1) production of phosphate as a result of the decomposition of organic matter. According to Taiwo [2] and Ogunfowokan [22], "organic matter decomposition in surface water produces inorganic nutrients such as ammonia, nitrate and phosphate with resulting effects of eutrophication and other serious ecological problems of such water body"; 2) the use of phosphate based fertilizer during the 2006 rice planting season might have resulted in the increased in phosphate load at S_2; 3) nitrate may be the limiting factor in the river.

(**Table 1**) No specific trend was observed in the nitrate, phosphate, BOD and DO levels from S_1 to S_3. However, there were significant levels of concentration in the nitrate, phosphate and BOD levels. These are shown in the results for the Chi-square distribution (**Table 2**). The concentrations of analysed parameters are shown to be significant at the 5 per cent (5.99) confidence limit.

(**Table 3**) A correlation between the statistically analysed parameters (5 per cent confidence limit) was shown with the strongest correlation observed between the BOD and DO (IrI = 0.9, $r^2 > 0.999$) and the weakest between BOD and nitrate (IrI = 0.3, $r^2 > 0.999$). A negative correlation was established between nitrate and phosphate concentrations. An increase in BOD and an expected drop in DO levels observed in the river at S_2 could suggest higher levels of decaying organic matter during the time of the study. As a result of the water becoming anaerobic due to oxygen depletion in water bodies, fish could die and an increase in BOD concentration signifies organic load [2]. Also, Adelekan [21] noted that BOD is a common measure of water quality and it reflects the degree of organic matter pollution of a water body.

The F-test (**Table 4**) shows that 0.92 is less than the critical value of 5.14 (5 per cent confidence limit) with the coefficient of variation calculated as 8.2 per cent. Less than 10 per cent contribution.

3.2. Heavy Metals Concentration

There was a 22.9 per cent drop in manganese concentration and a 14.8 per cent increase in lead concentration from S_1 to S_2. A 14.8 per cent increase in lead concentration at S_2, could suggest the presence of lead in the wastewater discharged from the rice farms. Perhaps from the use of an underground lead pipe network (for wastewater drainage) connected to a disused gravity irrigation system situated within Adarice farmlands. Agarwal [23] and Silambarasan [24] noted that problems exist in areas with soft slightly alkaline water which may dissolve lead from lead pipes. Adelekan [21] suggests that as the pH levels drop below 7.0; corrosion of water pipes may occur, resulting in the release of metals into drinking water.

A very high significant value of x^2 was established for Pb concentrations and non-significant values for Fe and Mn (**Table 2**). Also, values of IrI < 1 and > 0 (**Table 3**), indicate evidence of a correlation existing between the heavy metals with the strongest correlation observed between Pb and Fe (IrI = 0.99 $r^2 > 0.999$) and the weakest between Pb and Mn (IrI = 0.24, $r^2 > 0.999$). This could suggest a common source. The mean concentration of heavy metals showed the highest concentration to be at S_3 (**Figure 2**) suggesting 1) there could be other sources of heavy metals in the river besides the suspected agricultural wastewater from point source at S_2. 2)

Table 1. Surface water analysis result for the Obinna River.

Parameter	Unit	S_1	S_2	S_3	WHO standards
Physical analysis					
Odour		Nil	Nil	Nil	-
Colour	Hazen	70	70	70	-
pH value		6.5	6.5	6.5	6.5 - 9.0
Conductivity	$\mu s/cm^2$	2000	2000	2200	1000
Chemical analysis					
Acidity	mg/L CaCO$_3$	250	250	250	-
Alkalinity	mg/L CaCO$_3$	275	270	250	30 - 500
Total solids	mg/L	12	10	13	
Dissolved solids	mg/L	5	4	6	500
Suspended solids	mg/L	7	6	7	-
Calcium	mg/L	8.81	8	8.81	75
Magnesium	mg/L	0.51	0.49	0.51	Not greater than 30
Total hardness	mg/L CaCO$_3$	9.32	8.49	9.32	100 - 200
Sodium	mg/L	70	55	80	200
Potassium	mg/L	95	100	90	12
Iron	mg/L	0.001	0.001	0.1	0.3
Manganese	mg/L	1.53	1.18	1.47	0.1 - 0.5
Lead	ppm	18.9	21.7	39.7	0.01
Chloride	mg/L	354.6	351	343.9	250
Sulphate	mg/L	245.8	156.5	112.1	250
Nitrate	mg/L	0.04	0.03	0.03	50
Phosphate	mg/L	5	7.21	3.92	-
COD	mg/L	184	186	172	-
DO	mg/L	0.71	0.5	0.2	-
BOD	mg/L	184.71	186.5	172	-
Microbial analysis					
E-Coli/100ml	per 100 mL	Nil	Nil	Nil	Nil
Coliform	per 100 mL	Nil	3	2	Nil
Total plate count @35˚C after 24 hours		42	78	62	Nil

[*]BOD—biochemical oxygen demand, COD—chemical oxygen demand, DO—dissolved oxygen (Data adapted from [34]).

Table 2. Chi-square distribution.

Parameter	Result (X^2)
Nitrate	149.8
Phosphate	891.5
BOD	2286.38
DO	3.58
Iron	0.726
Manganese	4.92
Lead	240220.66

Table 3. Coefficients of linear Pearson's correlation IrI in surface water considering all samples from the Obinna River.

	Nitrate	Phosphate	DO	BOD
		Non Metals		
Nitrate	1	$-0.9^{n.s}$	0.7^*	0.3^*
Phosphate		1	0.4^*	0.8^*
DO			1	0.9^*
BOD				1

	Iron	Manganese	Lead
		Heavy Metals	
Iron	1	0.35^*	0.99^*
Manganese		1	0.24^*
Lead			1

n. s, not significant ($r^2 > 0.999$), *Significant Correlation ($r^2 > 0.999$).

Table 4. Difference in the mean concentrations of water samples.

Source of variation for the non-metals	Sum of squares	Degrees of freedom	Variance estimate for the non-metals
Between water samples	14787.56	2	14787.56/2
Within water samples	72318.92	9	72318.92/9
Total	87104.4	11	
Source of variation for the heavy metals	**Sum of squares**	**Degrees of freedom**	**Variance estimate for the heavy metals**
Between water samples	86.88	2	86.88/2
Within water sample	1528.7	6	1528.7/6
Total	1615.58	8	

there may have been some increase in pollution load downstream at S_3 perhaps, due to the movement of suspended and dissolved materials.
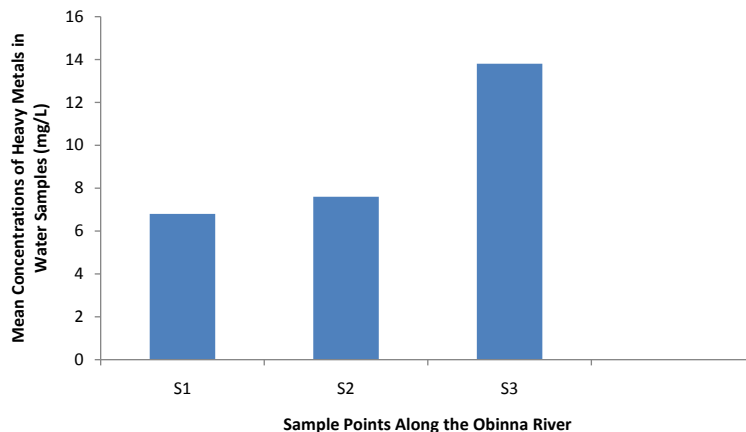
(**Figure 2** and **Figure 3**) The mean concentrations of heavy metals in the water samples indicate $S_1 = 6.8$ mg/L, $S_2 = 7.6$ mg/L and $S_3 = 13.8$ mg/L and also, iron (Fe) = 0.34 mg/L, manganese (Mn) = 1.40 mg/L and lead (Pb) = 26.8 mg/L. At S_3, 39.7 ppm or mg/L of lead contributed to the mean concentration of heavy metals (13.8 mg/L) with lead concentrations increasing from S_1 to S_3 (**Table 1**). According to Merhotra *et al.* [25] and Chakravaty *et al.* [26] "where stagnant condition prevails at the bottom of a river, the dissolved oxygen is completely removed.

As a result, free metallic complexes are formed which influence the solubility of metal "lead" by forming insoluble complexes. These complexes tend to strip the water of its metal content and enrich the bottom sediments with the metal". Near anaerobic conditions were observed at all points in the river (**Table 1**) with a decrease in concentration from upstream at S_1 to downstream at S_3.

It can be observed (**Figure 3**) that there was a trend in the increase in heavy metal concentrations along the river from upstream at S_1 to downstream at S_3 as follows Fe < Mn < Pb. The variance estimates (**Table 5**) show no significant change in the water quality as a result of the heavy metals present in the water samples. The coefficient of variation (**Table 5**) also shows less than 10 per cent (4.4 per cent) contributions from analysed parameters to the surface water.

Manganese is an essential metal that at excessive levels in the brain produces extra pyramidal symptoms similar to those in patients with Parkinson's disease [21] [27], and decreased learning ability in school age children and increased propensity for violence in adults [21] [28].

Lead is a particularly dangerous metal which has no biological role [21] [29]. Lead is a cumulative toxicant

Figure 2. Variations in the mean concentrations of heavy metals in water samples.
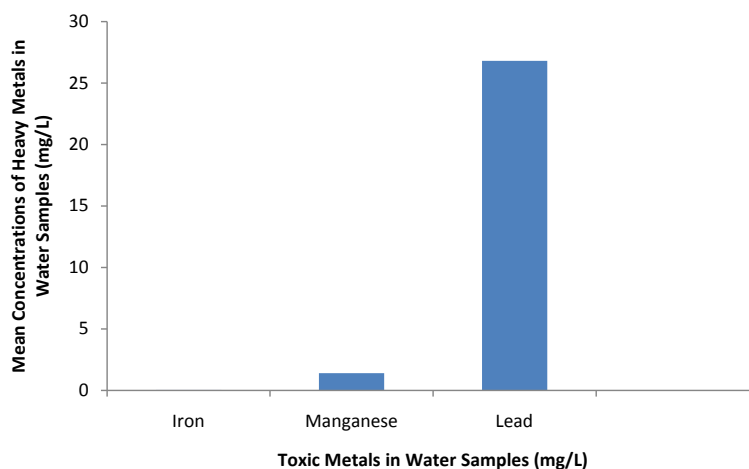
Figure 3. Variations in the mean concentrations of heavy metals in water samples.

Table 5. Standard deviation of analysed parameters.

Parameter (mg/L)	S_1	S_2	S_3	Mean value	Grand mean	variance	Standard deviation (°)
Nitrate	0.04	0.03	0.03	0.03			
Phosphate	5	7.21	3.92	5.38			
DO	0.71	0.5	0.2	0.47			
BOD	184.71	186.5	172	181.07			
Mean value	47.62	48.56	44.04		11.69	0.92	0.96
Iron	0.001	0.001	0.1	0.034			
Manganese	1.53	1.18	1.47	1.4			
Lead	18.9	21.7	39.7	26.8			
Mean value	6.8	7.6	13.8		9.4	0.17	0.41

that affects multiple body systems, including the neurological, haematological, gastrointestinal, cardiovascular and renal systems. Chronic exposure commonly causes haematological effects, such as anaemia, or neurological disturbances, including headache, irritability, lethargy, convulsions, muscle weakness, ataxia, tremors and paralysis. Acute exposure may cause gastrointestinal disturbances (anorexia, nausea, vomiting, abdominal pain), lepatic and renal damage, hypertension and neurological effects (malaise, drowsiness, encephalopathy) that may lead to convulsions and death [30] [31].

Iron has an essential role as a constituent of enzymes, such as cytochromes and catalase, and of oxygen transporting proteins, such as haemoglobin and myoglobin. In fresh waters, iron is also an important nutrient for algae and other organisms. Due to its high abundance within the earth crust, Iron is ubiquitous in all fresh water environments and often reaches significantly higher concentrations in water and sediments than other trace metals. High iron concentration in fresh waters has long been considered a problem. In domestic use, iron-enriched waters may induce rust formation on plumbing fixtures, the staining of laundry and a metallic taste in drinking water. The mining of iron rich ores has caused the degradation of many river ecosystems [24] [32]. Excess of iron will also influence the presence of bacteria (Iron reducing) in fresh water. It affects target organs like liver, cardio vascular system and kidney [24] [33].

4. Conclusion

The results showed a level of significance for the chi-square distributions and correlation coefficients while the ANOVA recorded conflicting results. Statistically, there was no significant change in the surface water quality of the river as a result of iron and manganese concentrations. However, the presence of values of some parameters above WHO standard, indicates pollution of the river. It can be inferred that Obinna River recorded significant change in water quality of the river as a result of fertilizer leachates flushing into the river.

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