Physicochemical Characteristics and Heavy Metal Levels of Four Rivers in Nkanu West and Nkanu East Local Government Areas of Enugu State Nigeria

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Authors’ contributions
This work was carried out in collaboration among all authors. The authors designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. The authors managed the analyses of the study and the literature searches. All authors read and approved the final manuscript.

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ABSTRACT
The physicochemical properties and the concentrations of heavy metals of water samples collected from four different rivers of Nkanu east and west Local Government Areas of Enugu of state Nigeria were investigated because of the prevalent water borne diseases in these localities attributable to the drinking of contaminated water. The water samples were collected from different sites of Esu, Umuekwe, Umuobeagu and Atafu rivers and their physicochemical properties and heavy metal contents were measured. Sampling Stations were selected; samples were collected avoiding contamination from the selected sites in same season, from same depth. On site measurement of...
parameters was done with the same instruments. Rests of the parameters were measured in Laboratory. Lead (Pb) was present in Esu, Umuekwe, Umuobeagu and Atafu rivers at a concentration of 0.14, 0.03, 0.00 and 0.16 mg/L respectively; Zn was only detected in Esu and Umuobeagu at 0.07 and 0.01 mg/L respectively and cadmium (Cd) concentrations of 0.14, 0.14, 0.08 and 0.08 mg/L respectively. Iron was detected in only Umuekwe river having 0.17 mg/L and Atafu river having 0.21 mg/L while Ni was detected at 3.01, 4.20, 1.20 and 3.83 mg/L respectively. Only Atafu river had Cr at 0.01 mg/L, only Esu river had Co content at 0.05 mg/L, Mn content in Esu, Umuekwe, and Umuobeagu was found to be 0.01, 0.02 and 0.02 mg/L respectively with Atafu river having none. Hg concentration was found to be 0.57, 0.06, 0.42 and 0.82 mg/L for Esu, Umuekwe, Umuobeagu and Atafu rivers respectively. The concentrations of Pb and Cd were higher in all the four samples especially in Esu river as a result of its closeness to construction sites and refuse dump and the concentrations were above the acceptable limits of WHO standard of 0.010 and 0.005 mg/L respectively for drinking water while Hg, Fe, and Ni were found within the W.H.O limits of 0.001, 3.000 and 0.100 mg/L respectively. The rest were below the standard, thus confirming conclusively that the rivers are polluted with the presence of heavy metals.

**Keywords:** Physicochemical properties; heavy metals; Nkanu east LGA; Nkanu west LGA; Enugu State; Nigeria.

### 1. INTRODUCTION

Environmental degradation due to pollution in rural area is pervasive, accelerating and unabated [1]. In developed countries, a lot of resources have been used to ensure that there is cleaner air, drinking water, sewage treatment, safe food laws and food refrigeration [2]. It is important to note however that even a very small concentration of persistent pollutants may cause irreparable damage to the ecosystem. Organisms susceptible even to low concentration may get eliminated [3]. The major sources of pollution include; burning fossil fuel in engines, waste disposal, accidental spills of chemicals from factories and use of agricultural chemicals.

![Map of Nkanu land indicating the location of water sources of study](image)

**Fig. 1. Map of Nkanu land indicating the location of water sources of study [9]**

*Key: R1= Umuobeagu, R2= Atafu, R3= Umuekwe, R4= Esu*
on farms which is the main activity in nkanu communities [4]. The most common environmental pollutants in the world are chemical elements such as heavy metals [5]. The presence of heavy metals at trace level and essential elements at elevated concentration causes toxic effects if exposed to human population [6]. Food chain contamination by heavy metals has become a burning issue in recent years because of their potential accumulation in bio systems through contaminated water, soil and air [7]. Research findings indicate that application of heavy doses of fertilizer, pollute ground water by nitrates and heavy metals through leaching and this affects the quality of water [8].

In spite of these regulations, there is still uncertainty as to the nature and extent of heavy metal pollution in Nkanu river areas. Thus, there is little information available on the level of heavy metals in the surface or near-surface soil in areas associated with water activities in Nkanu. A detailed study of lead-zinc water and soil areas could uncover the inherent danger posed to the communities where there are available. Heavy metal pollution could constitute serious environmental and health hazards in such communities.

The area of study is Nkanu East and Nkanu West Local Government Area in Enugu State, Nigeria. Nkanu East borders Ebonyi State to the east and its Headquarters is Amagunze. It is a rural area with a population of about 148,774 and land mass of approximately 795 km$^2$. Nkanu West has its Headquarters at Agbani. It has an area of 225 km$^2$ and a population of 146,695 [9]. The major occupation in these areas is farming.

This research work will not only enlighten the public as well as manufacturing industries on the pollution potentials and hazards of heavy metals and other chemical elements in water and soil but will also sensitize them on the level of pollution and the appropriate pollution control measures to adopt.

2. MATERIALS AND METHODS

2.1 Materials

Metter toledo compact seven pH meter, metter toledo compact seven electrical conductivity meter, conical flask, burette, evaporating dish, dessicator, bunsen, burner, filter paper, weighing balance, atomic absorption spectrophotometer.

2.2 Reagents

Buffer solution, eriochrome black T, EDTA (ethylenediaminetriacetic acid), indicator, silver nitrate solution, sodium hydroxide solution.

2.3 Methods

2.3.1 Sample collection

Water samples were collected from four rivers located in various villages in Nkanu East and Nkanu West Local Government Areas, in Enugu State, South-east of Nigeria. The villages are Amurri, Agbani, Umuze and ugbawka as shown in Fig. 1 and Table 1. The water samples were collected from the part of the river from which the villagers usually collect water and the samples were collected from different depths during monsoon. The samples were taken in new 2-litre polyethylene cans which were rinsed severally with distilled water, and finally with the water sample. The labeled cans were corked immediately and transported to the laboratory.

2.3.2 Physicochemical analysis

2.3.2.1 pH

Metter Toledo Compact Seven pH meter was used for the determination of pH. 20 ml of water sample was measured into a 25 ml sample cell. The sample cell was taken to the pH meter and the reading taken [10].

2.3.2.2 Electrical conductivity

Metter Toledo Compact Seven electrical conductivity meter was used. 20 ml water sample was measured into a 25 ml sample cell. The cell was taken to the electrical conductivity meter and the reading was taken [11].

2.3.2.3 Total hardness

Preparation of Reagent
- Buffer solution (pH 10): 57 ml of concentrated NH$_4$OH was added to 6.75g NH$_4$Cl. The resulting solution was dissolved and diluted to 100 ml with distilled water.
- Eriochrome black T: 0.5 g of Erio T powder was added to 4.5 g of hydroxylamine hydrochloride and dissolved in 100 ml of
95% ethyl alcohol. - 0.01 M EDTA: 3.723 g of the disodium salt was dissolved in 1 liter of distilled water.

### Procedure

Water sample (50cm$^3$) was measured into a conical flask and 1cm$^3$ buffer solution of NH$_3$ was added followed by addition of 3 drops of erochrome Black T indicator was also added and solution stirred properly. 0.01 M EDTA was titrated against the solution until the last reddish tinge disappeared leaving a blue colour at the end point. The volume of EDTA used was recorded.

### Calculation

Hardness (EDTA) = \[
\frac{\text{volume of titrants} \times 100}{\text{volume of sample}}
\]

Where A = average volume of 0.01M EDTA used, B = CaCO$_3$ equivalent to 1.00 ml EDTA titrant or titre value in ml sample volume of water sample used [12].

#### 2.3.2.4 Chloride

**Preparation of Reagent**

- K$_2$Cr$_4$ indicator: 50 g K$_2$CrO$_4$ was dissolved in a little distilled water. Silver nitrate solution was added until a definite red precipitate was formed. The solution was allowed to stand for 12 h, filtered and diluted to 1 liter with distilled water.
- Standard AgNO$_3$ (0.0141 N): 2.395 g of AgNO$_3$ was dissolved in distilled water and diluted to 1000 ml with distilled water.

**Procedure**

Water sample (100 cm$^3$) was measured into 250cm$^3$ erlynmeyer flask. The pH of the water was adjusted to 8.0 using sodium hydroxide solution. 10cm$^3$ of 0.1M potassium chromate was added to the solution. The mixture was then titrated with 0.014M AgNO$_3$ solution until the colour change from colourless to pinkish yellow as the end point [13].

Chloride Content (MgL$^{-1}$) =

\[
\frac{\text{Titre value} \times \text{Molarity} \times 35460}{\text{volume of sample}}
\]

Where 35460 = Chloride Constant

#### 2.3.2.5 Total Dissolved Solid Determination (TDS)

**Procedure**

Evaporating Dish was weighed and later 100cm$^3$ of the water sample was introduced into the weighed dish and dried in an oven operated at 103$^\circ$C for the proper drying for 1 hour. After drying it was transferred into a dessicator and left to cool for 1 hour. The dish was finally weighed with its content. The difference in weight gives the weight of the total dissolved solids of the sample [14,15].

#### 2.3.2.6 Total Suspended Solid (TSS)

**Procedure**

Water sample (100cm$^3$) is passed through a filter paper to remove the suspended solid in the sample and heated to dryness. Evaporating dish was weighed and 100cm$^3$ of the water sample was introduced into the weigh dish and dried in an oven operated at 103$^\circ$C for the proper drying for 1 hour. After drying it was transferred into a desiccator and left to cool for 1 hour. The dish was finally weighed with its content. The difference in weight gives the weight of the total dissolved solids of the sample [14,15].

Total Solid (TS) = Total dissolved solid (TDS) + Total suspended solid (TSS)

#### 2.3.2.7 Sulphate

**Preparation of Reagent**

Conditioning reagent: 50 ml glycerol was mixed with a solution of 7.5 ml concentrated HCl, 75 ml distilled water, 25 ml absolute ethanol and 18.75 g NaCl.

**Procedure**

Sulphate was determined using turbidimetry method. 100 ml of sample was measured followed by the addition of exactly 5.0 ml conditioning reagent. The solution was mixed thoroughly using magnetic stirrer and stirring bar. As the stirring continued, 0.2 g of BaCl$_2$ crystals was added and the solution was stirred for 1 minute at constant speed. After one minute, the sample was placed in a 5 cm cuvette and the absorbance was measured at 420 nm after exactly 4 min [16].
2.3.3 Determination of levels of heavy metals in water sample

Procedure

A standard solution of the metal to be obtained was prepared in order to obtain the calibration graph on the AAS. The sample to be analyzed was transferred into a sample cell. A capillary tube on the AAS was inserted into the sample which absorbed the sample and heats it up to its gaseous state. The result on the AAS was then recorded [17].

3. RESULTS AND DISCUSSION

The variation in the quality of the sampled rivers in Nkanu may have been caused by a number of factors, which ranges from natural to human factors as well as location of the rivers. However, the result of the laboratory water analysis only incorporates the tested parameters which include pH, acidity, electrical conductivity, total solid, total dissolved solids, total suspended solids, dissolved oxygen, biological oxygen demand, chloride, total hardness, nitrate, sulphate, lead(Pb), cadmium(Cd), chromium(Cr), nickel(Ni), cobalt (Co), iron(Fe), zinc(Zn), manganese(Mn), mercury(Hg), copper(Cu).

3.1 pH

The pH of water samples from the study area ranges from 4.7–5.1 excluding the Esu river having 6.7 which conforms to WHO standard for drinking water [18] while the rest shows weak acidity to neutral based on WHO standard.

3.2 Electrical Conductivity

Electrical conductivity of the water sample ranges from 139.3-1414 mg/L which shows that river Esu and Umuekwe is above WHO standard and river Umuobeagu and Atafu are below standard.

| Sample Rivers | Results (mg/L) | WHO standard (mg/L) | Remarks       |
|---------------|----------------|---------------------|---------------|
| Esu           | 6.71           | 6.5-8.5             | Within standard |
| Umuekwe       | 4.75           |                     | Below         |
| Umuobeagu     | 5.15           |                     | Below         |
| Atafu         | 5.13           |                     | Below         |

![Fig. 2. Comparative charts for pH results](image-url)

Table 1. pH result

| Sample Rivers | Results (mg/L) | WHO standard (mg/L) | Remarks      |
|---------------|----------------|---------------------|--------------|
| Esu           | 1414           | 500                 | -914         | Above         |
| Umuekwe       | 1180           |                     | -680         | Above         |
| Umuobeagu     | 139.3          | 360.7               | Below        |
| Atafu         | 379            | 121                 | Below        |
3.3 Total Hardness

Total hardness ranges from 5.20 mg/L – 16.4 mg/L which implies that the water samples are very moderate and can be used for domestic purposes because it will foam when used for laundry according to water hardness scale [19].

| Sample Rivers | Results (mg/L) | WHO standard (mg/L) | Level of variation | Remarks |
|---------------|----------------|---------------------|--------------------|---------|
| Esu           | 16.40          | 20.00               | 3.60               | Below   |
| Umuekwe       | 5.20           | 14.80               | 9.60               | Below   |
| Umuobeagu     | 5.40           | 14.60               | 9.20               | Below   |
| Atafu         | 12.40          | 7.60                | 4.80               | Below   |

Table 3. Total hardness result

3.4 Chloride

Chloride concentration of the water samples ranges from 9.9 mg/l - 23.3 mg/l. It implies that the water samples are portable according to the WHO Standard for drinking water. Excessive chlorine of 100 mg/l impacts salty taste [19].

Fig. 3. Comparative chart for electrical conductivity result

Fig. 4. Comparative chart for total hardness result
Table 4. Chloride results

| Sample Rivers | Results (mg/L) | WHO standard (mg/L) | Level of variation | Remarks |
|---------------|----------------|---------------------|--------------------|---------|
| Esu           | 23.33          | 25.00               | 1.67               | Below   |
| Umuekwe       | 19.33          |                     | 5.67               | Below   |
| Umuobeagu     | 9.92           |                     | 15.08              | Below   |
| Atafu         | 10.92          |                     | 14.08              | Below   |

Fig. 5. Comparative chloride result

3.5 Total Dissolved Solids (TDS)

The variation in total dissolved solids content of the sampled rivers in Nkanu reveals a very low range in values, as shown in table. Ranging from 10 mg/L-20 mg/L, it shows that the water is portable according to water test classification [19].

3.6 Total Suspended Solids (TSS)

The value of TSS ranges from 10 mg/L-30 mg/L which shows that the TSS content of Nkanu River is within the WHO Standard.

3.7 Sulphate

The sulphate content of the water samples ranges from 23.70–34.96 mg/L which shows that the river conforms to WHO standard.

3.8 Lead (Pb)

The concentration of lead in the rivers exceeds the WHO standard excluding Umuobeagu which has no lead content, river Esu, Umuekwe and Atafu river has 0.14 mg/L, 0.03 mg/L and 0.16 mg/L respectively. As regards to the presence of lead in rivers poses a great threat to the health. The presence may affect gastro intestinal tract, kidney and the central nervous system, for example when children are exposed to lead, they suffer from impaired development, lower IQ shortened attention span, hyperactivity and mental deterioration. In adults it leads to decrease reaction time, loose of memory, nausea, and weakness of joint and failure of reproduction.

Table 5. Total dissolved solids (TDS) result

| Sample Rivers | Results (mg/L) | WHO standard (mg/L) | Level of variation | Remarks |
|---------------|----------------|---------------------|--------------------|---------|
| Esu           | 10.00          | 25.00               | -15.00             | Below   |
| Umuekwe       | 10.00          |                     | -15.00             | Below   |
| Umuobeagu     | 20.00          |                     | -5.00              | Below   |
| Atafu         | 10.00          |                     | -15.00             | Below   |
### Table 6. Total suspended solids (TSS) result

| Sample Rivers | Results (mg/L) | WHO standard (mg/L) | Level of variation | Remarks |
|---------------|----------------|---------------------|--------------------|---------|
| Esu           | 20.00          | 30.00               | -10.00             | Below   |
| Umuekwe       | 10.00          | 20.00               | -10.00             | Below   |
| Umuobeagu     | 10.00          | 20.00               | -10.00             | Below   |
| Atafu         | 30.00          | 0.00                | 30.00              | Within  |

### Table 7. Sulphate results

| Sample Rivers | Results (mg/L) | WHO standard (mg/L) | Level of variation | Remarks |
|---------------|----------------|---------------------|--------------------|---------|
| Esu           | 28.60          | 50.00               | 21.40              | Below   |
| Umuekwe       | 25.32          | 24.68               | 26.30              | Below   |
| Umuobeagu     | 23.70          | 15.04               | 15.04              | Below   |
| Atafu         | 34.96          | 0.00                | 34.96              | Below   |
Fig. 8. Comparative chart for sulphate result

Table 8. Lead (Pb) result

| Sample Rivers   | Results (mg/L) | WHO standard (mg/L) | Level of variation (mg/L) | Remarks |
|-----------------|----------------|---------------------|---------------------------|---------|
| Esu             | 0.14           | 0.01                | -0.13                     | Above   |
| Umuekwe         | 0.03           |                     | -0.02                     | Above   |
| Umuobagu        | Nil            |                     | -Nil                      | Below   |
| Atafu           | 0.16           |                     | -0.15                     | Above   |

Fig. 9. Comparative chart for lead (Pb) result

3.9 Cadmium (Cd)

The concentration of Cd in the river ranges from 0.08 mg/L to 0.14 mg/L which exceeds the WHO standard 2008 [20]. This poses a great threat to the rivers. Excess Cd causes cardiovascular diseases, renal problems, severe pain in the joint, kidney and lungs; it affects the sperms and also reduces birth weight, liver dysfunction, nausea, cramps and loss of consciousness.
Table 9. Cadmium (Cd) result

| Sample Rivers | Results (mg/L) | WHO standard (mg/L) | Level of variation (mg/L) | Remarks |
|---------------|----------------|---------------------|--------------------------|---------|
| Esu           | 0.14           | 0.01                | -0.13                    | Above   |
| Umuekwe       | 0.14           |                     | -0.13                    | Above   |
| Umuobeagu     | 0.08           |                     | -0.07                    | Above   |
| Atafu         | 0.08           |                     | -0.07                    |         |

3.10 Cobalt (Co)

Esu river has 0.05 mg/L concentration of cobalt with the other rivers having none, this is below WHO standard 2008 [20]. Cobalt is important in humans in minute quantity because it’s part of vitamin B\textsubscript{12} which is essential component for human health.

The quality of surface waters in Nkanu and environs has been impaired considering similar studies [21-23] and this poses a threat to the inhabitant. From the study, it was observed that the area studied was polluted and this led to the impairment of the quality of surface waters in these areas. The pollution were probably from agricultural farmlands along the banks of the rivers, construction and channeling of open servers to the rivers by the inhabitants, washing of breadfruit, oil palm nuts, fermented cassava and indiscriminate disposal of domestic wastes into the surface waters. In addition, natural factors such as sediments from dissolution of rock minerals during weathering [24,25].
Table 10. Cobalt (Co) result

| Sample Rivers | Results (mg/L) | WHO standard (mg/L) | Level of variation (mg/L) | Remarks |
|---------------|----------------|---------------------|---------------------------|---------|
| Esu           | 0.50           | 3.0                 | 2.95                      | Below   |
| Umuekwe       | Nil            | Nil                 | Nil                       | Below   |
| Umuobeagu     | Nil            | Nil                 | Nil                       | Below   |
| Atafu         | Nil            | Nil                 | Nil                       | Below   |

4. CONCLUSION

The physicochemical composition and heavy metal levels of four rivers in Nkanu west and Nkanu east local government areas of Enugu state Nigeria have been assessed. The physicochemical composition results for the total dissolved solid (TDS), electrical conductivity, total hardness, chloride, nitrate and sulphate were below the World Health Organization (W.H.O) standard while only the pH of Esu river and the total suspended solids (TSS) of Atafu river were found to be within W.H.O standard. The concentrations of Pb and Cd were higher in all the four samples especially in Esu river as a result of its closeness to construction sites and refuse dump and the concentrations were above the acceptable limits of WHO standard of 0.010 and 0.005 mg/L respectively for drinking water while Hg, Fe, and Ni were found within the W.H.O limits of 0.001, 3.000 and 0.100 mg/L respectively. The rest were below the standard, thus confirming conclusively that the rivers are polluted with heavy metals. The detrimental impact of this impairment of surface waters affects not only the physical, economic and social wellbeing of the people but also have fatal consequence on the aquatic organisms. A continued increase in the pollution level of the rivers will ultimately prove fatal to human life in the area studied, ultimately promote the continued accumulation of heavy metals and other chemical compounds in the rivers, which are fatal to human and aquatic life as studied. From the study it was observed that lead and cadmium exceeded the WHO standard for drinking water in river Esu, Umuekwe, and Atafu and in all the rivers studied for lead and cadmium respectively. These metals if not checked will result to ailments in the consumers. For example excess cadmium will lead to cardiovascular diseases, bone diseases, renal problems, severe pains in the joints, kidney and lung problems and also anaemia due to decrease of iron adsorption by intestines, affects sperm, reduces birth weight and a causal factor in cardiovascular diseases and hypertension and for Lead will lead to poisoning or even death, gastrointestinal tract, kidneys, and the central nervous system. Also children exposed to lead (Pb) suffer from impaired development, lower IQ, shortened attention span, hyperactivity and mental deterioration, then in the case of adults" decreased reaction time, loss of memory, nausea, insomnia, anorexia, weakness of the joints, failures of reproduction, irritation, and producing tumours. And as a result of the poor health facility in the study area more increase in pollution of these metals will lead to high death rate.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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