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EVALUATION OF THE PHYSICO-CHEMICAL PROPERTIES OF WATER SAMPLES FROM ATA/ EHIMIRI STREAM WATERSHED ECOSYSTEM IN UMUDIKE, ABIA STATE, NIGERIA

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ABSTRACT

A single factor experiment in a randomized complete block design with three replications was used to study the physico-chemical properties of water samples from four watershed locations within Ata/ Ehimiri Stream in Michael Okpara University of Agriculture Umudike, Nigeria. Water samples were collected in duplicates from the different sampling locations using white polyethylene bottles (DO-Dissolved Oxygen, and BOD-Biological Oxygen Demand) bottles according to Ademoroti, (1996) methods. The results showed the physico-chemical properties of the stream water within the watershed ecosystem, the turbidity and temperature contents of the four study locations were statistically similar. The NRCRI and Fish Farm locations had significantly the highest and least hardness contents. The CVM and Raphia palm sites had the highest and least ($p \leq 0.05$) conductivity values. The Fish Farm site had significantly the highest Total Suspended Solids (TSS). The statistically similar Total Dissolved Solids (TDS) of the water samples from the NRCRI and CVM locations were significantly higher than the similar TDS values of the Fish Farm and Raphia palm locations. The pH of the water samples at the NRCRI locations was` significantly higher than the statistically similar pH values of the Raphia palm, CVM and Fish Farm sites. The NRCRI and the Fish Farm sites had the highest and least ($p \leq 0.05$) acidity contents. The NRCRI location also had the highest alkalinity and Dissolved Oxygen (DO) contents. The water samples from the Raphia palm and NRCRI sites had significantly the highest and least Biological Oxygen Demand (BOD) contents respectively. The Cl^-, NO_3^-, SO_4^-, PO_4^{-3}, and Pb contents of the water samples are within the acceptable limits/ range of drinking water and for other human uses.

Keywords: Ehimiri stream, watershed, water sample, location

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INTRODUCTION

Watershed is the drainage basin, river basin, catchment or drainage divide, or the corridor of a river /stream (Bisong, 2001). Rivers and river systems are complex and intimately connected to and also affected by the characteristics of their surrounding watershed, the land that water flows over and under on its way to the river (Ejizu *et al*., 2014). A monitoring program and reliable estimation of quality of the surface water are necessary, as the, physical and biological composition of surface water are the prime factors of which the suitability of water, domestic, industrial or agricultural purposes depend (Adesakin *et al*., 2017)

Water quality problems are diagnosed by linking the cause of the resource problem to its source and then estimating the pollutant load, if possible (OEPA, 2015). Sometimes diagnosing a water quality problem is not as simple as linking a single problem to a single source. Many times, diagnosis is complicated by multiple sources linked to several pollutants like, sediment/siltation (sand, silt, and clay), cropland and forestry activities, pasture, stream banks, construction roads, mining operations, gullies, livestock operations and other land-disturbing activities (OEPA, 2015). Sediments may destroy fish habitat by: (a) blanketing spawning and feeding areas, (b) eliminating certain food organisms, (c) causing gill abrasion and fin rot, and (d) reducing sunlight penetration, thereby impairing photosynthesis (OEPA, 2015). Nutrients and toxic substances attached to sediment particles may enter aquatic food chains, cause fish toxicity problems, impair recreational uses or degrade the water as a drinking water source. The principal concerns in surface water are entry into the food chain, bioaccumulation, toxic effects on fish, wildlife and microorganisms, habitat degradation and potential degradation of public water supply sources (OEPA, 2015). Groundwater impacts are primarily related to water supply sources. Toxic Substances (heavy metals, oil and petroleum products) may enter surface waters either dissolved in runoff or attached to sediment or Organic materials and may also enter groundwater through soil infiltration (Udoessien, 2014). Groundwater impacts are primarily related to degradation of water supply sources. Organic materials (natural or synthetic) may enter surface waters dissolved or suspended in runoff. Natural decomposition of these materials may deplete oxygen supplies in surface waters.

Most watersheds contain a mixture of land use practices, including forestry and agriculture. Protecting water quality requires an integrated multi-sector approach to watershed management. Streams that course through agricultural lands are often devoid of vegetation in their riparian zones and runoff containing excess fertilizers, pesticides, animal wastes and soil segments enters surface waters unabated. Agroforestry technologies, like riparian forest buffers, have been shown to be effective in reducing water pollution from agricultural activities when they are well designed and properly utilized in a watershed (Dosskey, 2002). These buffers can stabilize channel and reduce the transport of runoffs to streams. Linked systems of upland and riparian tree-based buffer systems, designed in regards to other landscapes practices and features can optimize soil and water conservation in the watershed, along with other economic and social services (UNEP, 2011). Agroforestry practices are also being adopted to design best management practices to detain and treat storm water runoff from communities and restore ecological functions to watersheds.

According to (OEPA, 2015), water quality models are tools for simulating the movement of precipitation and pollutants from the ground surface through pipe and channel networks, storage treatment units, and finally to receiving waters. Water quality models can simulate conditions on a continuous basis or for a single event. Models can be applied to watersheds that have storm sewer networks, natural drainage or both. Models can predict the discharge of the water body and concentrations of pollutants for a given set of initial watershed conditions. Modelling is an important tool for watershed management in that, once calibrated, models can predict watershed conditions after changes in land use or best management practices have been implemented (OEPA, 2015). Water as one of essential component of the planet earth has been tempered with through human anthropogenic activities on daily basis. Due to these actions of man, the water quality is being contaminated or polluted, hence concerted effort needs to be adopted to improve and sustains it originality in our environment. This study focuses on physico-chemical properties of water samples from Ata/ Ehimiri Stream watershed ecosystem in Umudike, Abia State, Nigeria.

MATERIALS AND METHODS

Study Area

Ata Stream is a tributary of Ehimiri Stream and flows from Lodu-Ibeku through Umudike to join the Akwa Ibom River. The study area of the Ata/Ehimiri Stream watershed is Umudike in Ikwuano Local Government Area, Abia State, Nigeria. Umudike lies within the humid lowland rainforest on latitude 05^0 29^1N and longitude 07^0 33^1E. It is on an altitude of 122m above sea level. The mean annual climatic data of Umudike are as follows: maximum and minimum temperature, 32^0C and 23^0C respectively; rainfall, 2238mm; relative humidity, 65-80% (Source: Meteorological Station, National Roots Crop Research Institute (NRCRI), Umudike in 2012) Umudike's soil type is mainly sandy clay or sandy clay-loam (Source, Soils Division, NRCRI in 2012).

METHODS

A single factor experiment in a randomized complete block design (RCBD) with three replications was used to study the physico-chemical properties of water samples from four watershed locations within Ata/ Ehimiri Stream in Michael Okpara University of Agriculture Umudike, (MOUAU). Water samples were collected in duplicates from the different sampling locations using white polyethylene bottles (DO-Dissolved Oxygen, and BOD-Biological Oxygen Demand) bottles according to Ademoroti, (1996) methods. The bottles were rinsed with the water to be sampled prior to collection. Sufficient air spaces were left in the bottles, (except those for DO determination) to allow for expansion of the water at increased temperature. In all cases, sampling bottles were used directly by holding the bottles horizontally and allowing the bottles to flow in gently. The bottles were gradually being raised until the flow of water sample was sufficient. Water samples for DO and BOD were collected in brown glass stoppered bottles. In each case, the bottles were carefully filled without trapping air bubbles. For the DO samples (200ml each), 2ml of $MnCl_2$ solution was added, followed by the addition of 2ml alkali-iodide-azide reagent well below the surface of the liquid (water) using separate dropping pipettes. The excess solution was allowed to overflow. The bottle was stoppered with care to exclude air bubbles and mixed by inverting the bottles a number of times until clear supernatant water was obtained and precipitate was allowed to settle. The temperatures of the different water samples were determined *in situ* by dropping the mercury-in-glass Celsius thermometer (O°C -100°C) for about five minutes until a steady temperature was observed. pH paper was immersed in the water sampled and colour change was observed and compared with a standard. This was confirmed using a pH-meter (each model) standardized before use with a standard buffer solution of pH 4.0 (potassium hydrogen phthalate, 0.05M) and pH 9.2 (Borax buffer, 0.01M). The temperature setting on the meter was made before any measurement began. The electrodes were rinsed with deionized water and buffer solutions between samples before being immersed into water samples for about five minutes in each case. Measurements were made in the triplicates and the average values were recorded. Samples were then transferred to the laboratory for further analysis. The samples collected for analysis were preserved in the laboratory in order to prevent or retard the chemical and biological changes that could inevitably occur once the samples are removed from their sources. Four (4) white polyethylene bottles containing different water samples were kept in a refrigerator at 4-^{0}C- a temperature where bacteria are inactive in order to ensure the accuracy for acidity and alkalinity determinations. Four (4) white polyethylene bottles containing different water samples to be used for elemental and anionic determinations were filtered through a Whatman No. 42 filter paper to remove the suspended matter to samples. For elemental analysis, concentrated HNO_3 was added to pH 3 to maintain the oxidation state of the elements and to prevent metals from adhering to the walls of the containers. Also, four (4) incubator bottles containing the water samples were placed in an incubator in the dark (to prevent consumption of DO by algae in the sample) at 20^0C.

To each water sample contained in the BOD bottles, 2ml conc. HCl was added by allowing the acid to run down the neck of the bottle, restoppered, and mixed by gentle inversion until dissolution was complete and by making sure the iodine was uniformly distributed throughout the solution. 100ml of the solution was titrated against standard 0.0125 $MNa_2S_2O_3.5H_2O$ to a pale straw yellow colour. On the addition of 2 drops of starch indicator, the colour became blue, and this titration was continued by adding the thiousulphate solution drop wise until the blue colour disappeared.

Determination of Dissolved Oxygen (DO) using alkaline-azide modification of Winker method (Ademoroti, 1996)

Procedure:

Water sample was filled into a 250ml brown bottle $2cm^3$ of MnCl was added followed by 2 cm^3 of alkali-iodide (AL-KI) reagent just below the surface of the liquid. In additions to these two solutions, precipitation was formed and was allowed to settle until a clear supernatant was observed.

Two centimetres cube ($2cm^3$) of HCl was added to the liquid by allowing the acid to run down the neck of the bottle. This was restoppered, mixed by gentle inversion until dissolution is completed. A known volume needed was withdrawn for titration with 0.0125M $Na_2S_2O_3$ to give a pale straw colour (pale yellow). Two centimetres cube ($2cm^3$) of the starch solution was added to give a blue colour; titration continued by adding the thiousulphate solution drop wise until the blue-black colour disappeared

Calculation:

$$\text{Mg/l DO} = \frac{16{,}000 \times M \times V}{\frac{V_2}{V_1}(V_1 - 2)}$$

Where: M = Molarity of the thiousulphate

V = Vol. of thiousulphate needed for titration.

V_1 = Vol. of the bottle with stopper in place.

V_2 = Vol. of aliquot taken for titration.

When all the content of the bottle was titrated, the formula below was used

$$\text{Mg/I DO} = \frac{16{,}000 \times M \times V}{(V_1 - 2)}$$

(a) Temperature (O°C): A Celsius thermometer (mercury in glass centigrade thermometer O^0C-110^0C) was used to take the temperature. The thermometer was vertically immersed with the bulb containing the mercury in the water sample for about five (5) minutes. The reading was taken as the mercury rose to a steady state. The pH was taken at the site. **(b) Hydrogen Ion Concentration (pH) determination:** a pH meter model 3320 Jenway (electronic) was initially standardized using buffer solutions 4 and 9 respectively to serve as check for proper instrument response before sampling measurement. The electrode was rinsed with distilled water and then inserted in the water sample. The pH value was recorded on the meter scale at a steady point. After each determination, the pH sensing bulb was rinsed with distilled water before being used for the next determination. **(c) Turbidity-** apparatus: (Water checker U-10 Horiba) – measurement of the turbidity was done using water checker instrument. However, the water was filled to a standard level cup of the water checker to enhance the reading. The electrode was put into the water and the selector adjusted to turbidity position until a steady value appeared, indicating the turbidity of the water. 1mg/I = 1 unit turbidity. **(d) Conductivity:** Determination of conductivity was done using conductivity meter model: Suntex sc-120.

The electrode was properly rinsed with distilled water before talking the measurement. For every subsequent set of water determination, the electrode was rinsed at each interval. Data were obtained from the readings.

(e) Determination of Acidity (AOAC, 1984): Phenolphthalein alkalinity (PAK): fifty mills (50ml) of each water sample were measured into 250ml conical flasks. Three (3) drops of the phenolphthalein indicator were added in each case and the solution titrated with CO_2 free NaOH solution (0.02M) until the appearance of a faint pink colour (pH 8.3) was observed. This indicates the end point of the titration. Methyl orange acidity (MOA): To 50ml of waste water and effluent samples, three (3) drops of methyl orange indicator were added and the solution titrated with CO_2 free NaOH solution (0.02M) to the point. **(f) Determination of Alkalinity (AOAC, 1984):** Phenolphthalein alkalinity (PAK): fifty mills (50ml) of each water sample was measured into different (250ml) conical flasks. Three (3) drops of the phenolphthalein indicator were added until the solution remained colourless indicating a zero PAK. **(g) Total alkalinity (TA):** the addition of PAK and MOA expressed is $CaCO_3$. **(h) Determination of Total Suspended Solids (TSS)** according to Ademoroti (1996) methods: 50ml of each water sample was measured into different conical flasks. Five mills (5ml) of diluted H_2SO_4. (1:3) was added and the solution was quickly transferred to a steam bath to boil. The 15ml of 0.01M $H_2C_2O_4$ was added followed by a drop of MnO_4 (0.01M) from the burette until the solution turned pink. **(i) Determination of Total Dissolved Solid (TDS) (Ademoroti, 1996):** the Whatman filter paper No. 42 was dried to constant weight, cooled to room temperature in a desiccator and the weight noted. Fifty mills (50ml) of thoroughly mixed water sample was measured and filtered. The filtered residue was dried at a temperature of 103°C- 105°C in an oven for 30-40 minutes. The filter paper and the residue were cooled and weighed. **(k) Determination of Total Solids (TS)** (Ademoroti, 1996): the sum of TDS and TSS gave TS expressed in mg\l. **(l) Determination of Chlorine (Cl)** also according to Ademoroti (1996): To 25ml of each water sample, three (3) drops of 5%K_2CO_4 indicator were added to obtain the Cl content. **(m) Determination of Biological Oxygen Demand (BOD)** using AOAC (1984) method: the method for the determination of BOD was similar to that for DO, but in the BOD test, the water samples were kept in an indicator in the dark and preset at 20^0C for 5 days. After incubator, the DO test was repeated. **(n)** Determination of Ca, Mg, Zn, were also carried out using Ademoroti (1996) method: twenty-five mills (25ml) of each water sample were measured into 250ml conical flasks. 2ml of buffer solution was added. This was followed by the addition of two (2) drops of Eriohrome back T indicator. The rose-pink solution obtained was titrated with 0.01M EDTA until the colour changed to blue indicating the end point. The EDTA complexes with Ca, Mg and Zn. For Zn only, 25ml of each water sample was measured into 250m conical flasks; two drops of xylenol orange were added and the colour changed to yellow. Few crystals of hexamine were added until the yellow colouration turned pink solution was titrated with 0.01M EDTA until the colour returned to yellow. All the physico-chemical properties of water samples were also statistically analyzed using Fisher's LSD at $p \leq 0.05$ (Steel and Torrie, 1980) and Alika (2006).

RESULTS

Table1 showed the physical properties (temperature, hardness, conductivity, total suspended solids (TSS), total dissolved solids (TDS), turbidity) of water samples of Ata/ Ehimiri stream at four sampling locations in Umudike, Nigeria. Details of the results are stated below: (a) Temperature (^{O}C): The temperature values of the water samples at the various study locations were not significantly different from each other. (B) Hardness (mg l^-

^{1}): the NRCRI and Fish Farm locations had significantly the highest and least hardness contents. (c) Conductivity (µs): the College of Veterinary Medicine and Raphia palm plantation site had significantly the highest and least conductivity values respectively. (d) Total suspended solids (TSS) (mg l^{-1}): the water sample of the Fish Farm location had significantly the highest TSS. The statistically similar TSS contents of water samples of the College of Veterinary Medicine and the NRCRI locations had significantly the least results. (e) Total dissolved solids (TDS) (mg l^{-1}): the statistically similar TDS values of water samples at the NRCRI and College of Veterinary Medicine study sites were significantly higher than the similar ($p \geq 0.005$) TDS values of the Fish Farm and Raphia palm plantation sites. (f) Turbidity (Abs): the turbidity of the water samples of the various study locations were clear and were not significantly different from each other.

Table 1: Physical Properties of Water Samples of Four Study Locations in the Ata/ Ehimiri Stream Watershed Ecosystem in Umudike, Nigeria.

Locations	Temperature (^{0}C)	Hardness (Mgl^{-1})	Conductivity (µs)	TSS (Mgl^{-1}	TDS (Mg ^{1})	Turbidity (Abs)
NRCRI, Umudike	24.20	56.00	11.90	68.00	972.00	0.00
CVM, MOUAU	25.10	28.00	13.21	70.00	956.00	0.00
Fish Farm, MOUAU	25.20	24.00	12.40	85.67	928.00	0.00
Raphia palm Plantation, MOUAU	17.40	32.00	10.06	74.00	922.00	0.00
Mean	23.00	30.00	11.89	74.42	944.50	0.00
F-LSD (0.05)	NS	1.94	0.45	3.24	17.90	NS

NRCRI = National Root Crops Research Institute
MOUAU =Michael Okpara University of Agriculture Umudike
CVM = College of Veterinary Medicine, Michael Okpara University of Agriculture, Umudike

Table 2 showed the Chemical properties of pH, acidity, alkalinity, dissolved oxygen (DO), biological oxygen demand (BOD) and chemical oxygen demand (COD) of water samples of Ata/ Ehimiri Stream at four study locations in Umudike, Nigeria. **(a) pH:** the pH value of the water sample from the NRCRI study location was significantly higher than the statistically similar pH values of the water samples from the Raphia palm plantation, College of Veterinary Medicine and Fish Farm locations. **(b) Acidity:** the NRCRI and the Fish Farm study locations had significantly the highest and least acidity values respectively. **(c) Alkalinity:** the water sample of the NRCRI location had significantly the highest alkalinity value. The Raphia palm plantation and Fish Farm study sites had statistically similar alkalinity contents which were the least ($p \leq 0.05$) results. **(d) Dissolved oxygen (DO) (mg l^{-1}):** the water sample of the NRCRI study location had significantly the highest DO content. The DO value of the water sample of the Fish Farm site was higher ($p \leq 0.05$) than they DO content of the water sample of the Fish Farm location. However, the DO values of water samples of the Fish Farm and College of Veterinary Medicine sites were statistically similar. The College of Veterinary Medicine and Raphia palm plantation study locations also had similar ($p \leq 0.05$) DO contents. Raphia palm plantation site had lower ($p \leq 0.05$) DO values than NRCRI and Fish Farm locations.

(e) Biological oxygen demand (BOD) (**mg** l^{-1}**):** the water sample of the Raphia palm plantation and NRCRI locations had significantly the highest and least BOD contents respectively. **(f**) **Chemical oxygen demand (COD)** (**mg** l^{-1}**):** the water samples of the College of Veterinary Medicine and NRCRI study locations had significantly the highest and the least COD values.

Table 2: Chemical Properties of Water Samples of Four Study Locations in the Ata/ Ehimiri Stream Watershed Ecosystem in Umudike, Nigeria.

Locations	pH	Acidity (mg l^{-1})	Alkalinity (mg l^{-1})	DO (mg l^{-1})	BOD (mg l^{-1})	COD (mg l^{-1})
NRCRI, Umudike	6.45	64.00	40.00	17.66	6.50	14.08
CVM, MOUAU	6.18	52.00	34.00	16.03	7.85	18.56
Fish Farm, MOUAU	6.14	48.00	32.00	16.33	7.35	17.92
Raphia Palm plantations MOUAU	6.21	56.00	32.00	15.51	8.16	17.28
F-LSD (0.05)	0.11	2.26	1.76	0.57	0.18	0.21

NRCRI= National Root Crops Research Institute.
MOUAU =Michael Okpara University of Agriculture, Umudike.
CVM= College of Veterinary Medicine, Michael Okpara University of Agriculture, Umudike.

DISCUSSION

The pH values of the water samples at the various sampling locations were not acidic but were between 6.5-7.0 pH units for fresh water quality. This limit also is within the permissible limits of 6.5-8.5 for drinking and domestic water (WHO, 1984). It was also reported by SON (2007) that pH values above permissible limits have no adverse health impacts on the consumers. Therefore, since the surface water in the sampling locations were not acidic due to pH values, they could be suitable for domestic consumption. The non-significantly different (17.40^0C-25.20^0C) temperatures of the water samples in the four study locations were similar to the findings of Kalu (2004) at the Aba River in Aba, Nigeria. The temperatures are within the acceptable limits of water sample within the humid tropics (FEPA, 1991; WHO, 1984).

Also, the turbidity values of the sampling points are clear and suitable for drinking water and aquatic life (FEPA, 1991; Isirimah, 2002). This study therefore shows that the fresh water samples of the different sampling locations are suitable for domestic purposes and human consumption. The hardness contents (24.0-56.0 mgl^{-1}) of the sampling locations were relatively low compared with the WHO (2004) and NSDWQ (2007) compliance limits of between 150-500 mgl^{-1} for hardness contents in the water samples. However, SON (Standard Organization of Nigeria) (2007) observed that hardness of water has no adverse health impact, and that it is not one of the routine monitoring parameters. Total dissolved solids (TDS) (922.0-972.0 mgl^{-1}) from the sampling locations were proportional to the conductivity value of the sampling locations. The highest TDS values (972.0 mg

l^{-1}) obtained at NRCRI location indicate that the water sample at the NRCRI site contained more dissolved solid particles than the other water samples. The lowest TDS values (922.0 mg l^{-1} and 928.0 mgl^{-1}) which were obtained at the Raphia palm and Fish Farm sites respectively could be minimal due to self-purification and anthropogenic activities. However, the TDS values at all the point sources are within the permissible unit for drinking water (SON, 2007). The water sample in NRCRI site had lower TSS content than the other study locations. The high TSS content in the water sample of Fish Farm site could be attributed to insoluble solid particles depending on the level of dirt in the water source. However, the TSS contents of the different sampling locations are within the range recommended by NSDWQ (2007).

The conductivity of water sample within the study locations ranged between 10.6-13.21µs/cm and was lower than the 500.00µs/cm of the WHO (2004) water guidelines. Conductivity values are directly proportional to the levels of total dissolved solids in water. This is because electrical conductivity of water is a measure of its ability to transfer electrical current under specific conditions and the ability of the current being carried is directly proportional to the amount of dissolved salts in the water (Todd, 1980). The alkalinity contents of the stream/river samples which ranged between 32-40 mgl^{-1} were within the specification of WHO (1989) for fresh water quality. The BOD (6.50-8.16 mg l^{1}), COD (14.08-18.56 mg l^{1}), and DO (15.51-17.66 mg l^{1}) contents of water samples in the study locations are in line with the findings of Krebs (1978) who observed that increase in Organic matter and mineral salt water lead to an increase in biochemical processes of catabolism and anabolism. However, there are presently no limits to DO, BOD and COD contents for drinking water (FEPA, 1991).

CONCLUSION

The study has shown that physico-chemical properties of the stream water samples within the Ata/Ehimiri watershed ecosystem stream has good water quality that compared favourably with the established standards for drinking water quality and other domestic uses. This therefore recommends that the residents in local communities, housing estates and in urban areas close to watersheds should avoid dumping of refuse within areas of watershed. This feature will ameliorate water pollution and the ever increasing total suspended solids (TSS) in water bodies within watershed ecosystems. Regular or periodic research should be carried out especially on the water quality of the watershed ecosystem, including Ata/Ehimiri watershed ecosystem, since several communities within the stream/river watersheds utilize the water as drinking water

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