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ASSESSMENT OF MICROPLASTICS PHYSICAL AND CHEMICAL PROPERTY CONCENTRATION IN SURFACE STREAM WATER OF UYO METROPOLIS

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ABSTRACT: *Assessment of microplastics physical and chemical properties in surface stream water of Uyo metropolis was carried out at different stream locations within Uyo metropolis where waste plastics and microplastics are generated and disposed through runoff. Three stream water samples were used. GPS coordinates were taken, samples were taken accurately using volume bulk collection method into glass bottles and analyzed in the laboratory. A comparison approach was adopted with a control site to assess the level and concentration of microplastics physical and chemical properties present in the water surface. Water samples were collected, sieve to get the microplastic particles present and analyzed using standard procedures by Associations of Official Analytical Chemist and American Public Health Association. Data were analyzed statistically using ANOVA and Duncan multiple range tests for mean separation. Correlation analysis was done to check the differences in parameter's relationship. The mean value of the microplastic physical and chemical properties (proximate and ultimate analysis) ranges as follow Dominic Utuk and Uyo village road stream had %Carbon (12.67%-8.78%), Oxygen (83.89-21.67 %), Nitrogen (0.38-0.15%), Hydrogen (7.86-5.18 %), Sulfur (0.16-0.77 %) respectively. These were higher than the control site (3.22, 12.05, 0.05, 2.45, 0.03%). Ultimate assay for Dominic Utuk and Uyo village road stream recorded %Fixed carbon (19.85, 15.77), %ash (1.03, 2.09), %volatile matter (79.12, 82.14%), and %residual content (0.89, 0.71) higher than the control (4.23, 0.12, 17.15, 0.29%) respectively. Heavy metals and anions assessed showed that Lead, Cadmium, Mercury, Chromium, Arsenic and Chlorine and Bromine were higher in the two stream microplastic than that of the control site and WHO permissible limit for water. Correlation analysis shows a strong, positive and perfect relationship between some parameters measured. Contamination factor and pollution index also reveal possible contamination and pollution load these elements have which can affect negatively the water quality and marine organisms in it. The study therefore concludes that there is a huge negative impact of microplastics particles in the stream water of Uyo metropolis and therefore recommends a proper recycling, reuse and disposal method for plastic materials and microplastic substances in the environment.*

KEYWORDS: Anions, Contamination factor, Heavy metal, Microplastic, Pollution index Proximate and Ultimate Analysis.

INTRODUCTION

MICROPLASTICS are materials or products which originate from a vast range of polymers of high molecular mass (Bbayemi *et al.,*2018). These microplastics have broad applications temporally and spatially as a result of their durability, easy to produce, less expenses and relatively less weight. Recently in the decades past, there was tremendous increase in microplastic usage for a wide range of products. According to the Brussels European Commission (2013), global production of microplastic has increased from 1.5 million tons (Mt) per year in 1950 to 245 Mt in 2008 and still counting. Microplastic originated from plastics products comes from petroleum products just like refined gasoline from the same petroleum products. According to the Environmental Protection Agency, estimated production rate of plastic products and its particles account for about 8% of oil production rate globally (Merino and Ayer, 2018). This particle breaks down to form microplastics and microbeads in the soil and water and sometime are eaten by microorganisms to further break it to smaller particles. Other sources of microplastics are from cosmetic products, laundry water where cloth fibres particles are disposed of to the environment after use. This affects the soil and water quality, aesthetic views of the environment and possibly the food web. This, therefore, warranted the need to under study the environment so as to determine the concentrations of microplastics as a result of indiscriminate human disposal to the ecosystem. This study seeks to investigate the concentration of microplastics physical and chemical characteristics using proximate and ultimate analysis methods, heavy metals and anions content in studied water samples of Uyo metropolis. However, this research is needed to further fill in the knowledge gap of emerging microplastic pollutants in our environment.

LITERATURE/THEORETICAL UNDERPINNING

Microplastics in the world today are common. In 2014, the World Ocean was estimated to have between 15 and 51 trillion individual pieces of microplastic, with estimated weight of 93,000 and 236,000 metric tons (Ioakeimidis *et al*., 2016; Sebille *et al*., 2016). There is truly a staggering amount of microplastics particles inside our world's water bodies, as a debate of exactly the amount of microplastics present in the world's water bodies. A study conducted on the distribution of surface plastic debris in the Eastern Pacific Ocean helps to demonstrate how the concentration of plastics in the ocean is on the rise (Law *et al.,* 2014), though there have only been a few studies on microplastics present in freshwater ecosystems. According to Anderson (Anderson, *et al.,* 2016), microplastics are being detected in the world's aquatic environments increasingly. The first study on microplastics in freshwater ecosystems had an average of 37.8 fragments per square meter of microplastics in Lake Huron sediment samples which were published in 2011. Additional studies by (Ivleva *et al*., 2017) reported microplastic to be present in all the Great Lakes with an average concentration of 43,000 MP particle km. These particles get to the water and soil, breakdown into smaller particles called microplastics and their chemical constituent enters the soil and water thereby polluting it. Microplastics that get entangled with chemicals during the manufacturing process or absorbed from the surrounding environment brings a big concern regarding physical and chemical toxicity of the food chain. There is evidence regarding microplastic toxicity and epidemiology which is emerging in today's scientific research.

METHODOLOGY

Study Area

Microplastics physical and chemical property concentration in surface stream water was carried out in Uyo metropolis, the capital city of Akwa Ibom State. The city lies between longitudes $7^0 51'$ E and $7^0 59'$ E, and between latitudes $5^0 40'$ N and $5^0 59'$ N (fig. 1). According to Ituen and Nyah(2015), Uyo Capital City covers an approximate area of 188.024 km^2 with an estimated population of 305,961. Uyo metropolis envelops the entire Uyo, parts of Itu, Uruan, Nsit Ibom and Ibesikpo Asutan Local Government Areas in Akwa Ibom State (Etuk *et al.*, 2018). Urban expansion and economic growth lead to infrastructural development that extends to nearby local government areas of Itu, Uruan and Ibesikpo Asutan. Temperature of Uyo corresponds with that of the tropical humid climate and ranges between 26.2 ^{0}C and 35 ^{0}C with mean annual temperature of 28.4 ^{0}C (Ukpong 2009). The annual precipitation ranges from 2000-3000mm per annum. According to Etim and Okon, (2013), this rainfall regime received in most parts of the state encourages farming throughout the year. The occupations of the inhabitants reflect the economic activity of the residents. The settlements are majorly Ibibio though there are settlers from other ethnic groups. According to Etim *et al* (2006) the settlement pattern in Uyo is nucleated and being an administrative headquarters, majority of the residents are government employees and political office holders. These people also engage in farming activities and other commercial ventures within and around their urban residences as a means of augmenting and supplementing family income and food supplies (Etim *et al*., 2006). According to Usoro and Akpan (2006) sandstone hills and ravine are attributed to parts of Uruan and Uyo Local Government Areas while other sections of the study area are filled with low lying undulating sandy plains terrain (Ituen and. Nyah, 2015).

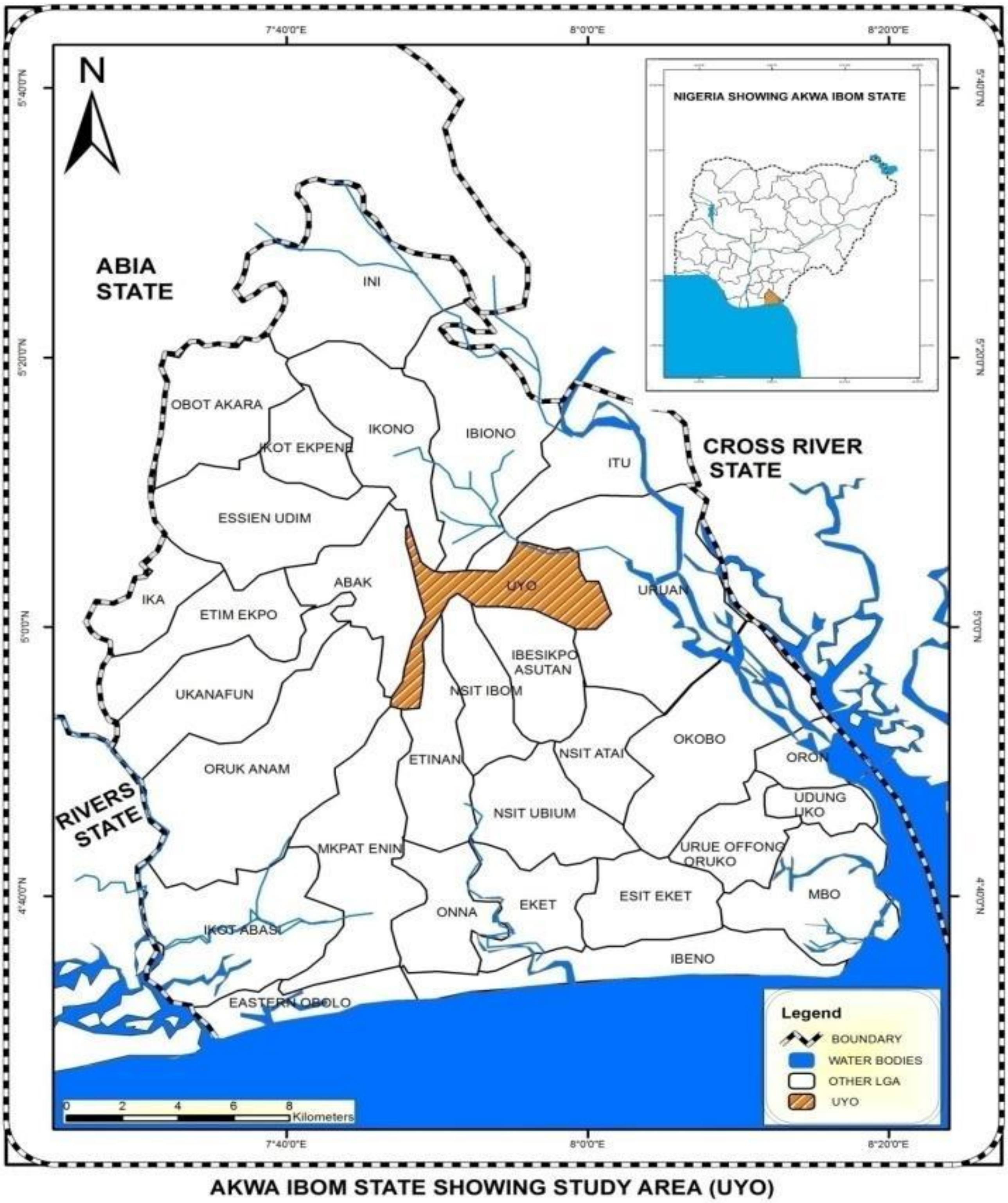

Fig. 1: Map of Akwa Ibom State Showing the Uyo LGA.

Sampling Location and Collection

Volume-reduced Bulk water samples approach method was used for sampling because it collects large quantities and areas of samples during sampling (Crawford and Quinn. 2017).

Water samples were taken from three stream sources within the metropolis where possible contamination occurs through runoff and outside the metropolis (control).

The samples were collected using a large bucket and storing the water in a large volume container. The GPS coordinates, wind speed, and wind direction (Table 1) were taken at the time of sampling. The sample volume at each location was a minimum of 10 litres. The bulk water samples were taken to the laboratory for analysis of microplastic polymer physical and chemical properties as described by (Hidalgo-Ruz *et al.*, 2012; Song et al., 2014). The samples were stored in a refrigerator at 4°C prior to analysis (Mamun *et al.,* 2011).

Water Sample Preparation and Laboratory Analysis.

The samples were directly poured through a sieve (stacked sieves), particles were visually sorted out from the debris. Micro particles bead/particles identified and sorted were analyzed for their physical and chemical characteristics.

Determination of Physical and Chemical Characteristics of Microplastic Identified Using Proximate and Ultimate Analysis Method.

After identification of microplastic particles from water samples, they were grinded for size reduction and analyzed further for their physical and chemical characteristics. The parameters and method used are as follows:

Physical Characteristic of Microplastics

Heating value: The heating value of plastic particles was calculated using the Dulong equation as Stated.

$$HV = 33801(C) + 144158[(H) - 0.125(O)] + 9413(S) \quad (1)$$

Where:

HV(kJ/kg) is a Heating Value whereas C, H, O and S are carbon, hydrogen, oxygen and sulfur content respectively in the dry basis. Higher heating value (HHV) is an important property which defines the quantitative energy content and determines the clean effective and efficient utilization of the plastic products according to (Othman *et al*., 2008).

pH value : the pH value of polymer identified and grinded samples were determined using Digital pH meter as described in recent study by (Othman *et al*., 2008).

***Moisture content*:** the percent moisture content of microplastic was determined by weighing the wet microplastic particles and drying the samples in an oven at 105°C for 1 hour using desiccators to a constant weight according (ASTM D3173) method. The percent moisture content was calculated as a percentage loss in weight before and after drying using Equation (2 and 3) (Othman *et al*., 2008).

% Moisture content =

[(Wet Weight – Dry Weight)/ Wet weight] x 100 (2)

Or

The percentage of moisture content (MC) was calculated as a fraction loss in weight of sample before and after drying.

M1=mass of empty crucible (g)

M2=mass of empty crucible + sample (g)

M3=mass of empty crucible + sample after heating (g)

Moisture content = M2 – M3

% moisture content = M2 - M3/ M2 - M1 x 100 (3)

Chemical Characteristics of Microplastic

Proximate analysis*:* The parameters analyzed include Residual Content (R), volatile matter (VM), Fixed Carbon (FC) and Ash Content (Ash). The method used was based on the ASTM Standard D 3172 as suggested by (Brunner,1994). The weights of dry samples were measured. (Othman *et al*., 2008).

Ultimate analysis: The parameter analyzed includes Carbon, Hydrogen, Sulphur and Oxygen Content. In this study, the equipment used is Elemental Analyzer (CHNS Analysis) model EA 1106 prepared by Thermo Quest Italian S.p.A. In this study, the equipment used was Elemental Analyzer (CHNS Analysis) model EA. The weights of dry samples were measured (Othman *et al*., 2008).

Neutron activation analysis: The parameter analyzed includes total chlorine and total bromine content using Trig Mk II Reactor, Rotary Rack, Pneumatic Transfer System and detector. For Total Chlorine determination, a short irradiation process was used and for total bromine, a long irradiation process was used. The weight of dry samples was measured (Othman *et al*., 2008).

Heavy metals Analysis*:* Heavy metals parameters include Cd, Cr, Hg, Pb and as were determined from the identified microplastic particles in the soil samples. They were determined after extraction by Flame Atomic Absorption Spectrometry in accordant with American Society for Testing and Material (2013) standard test method.

Determination of Ultimate analysis (Elemental Composition)

The combustible percentage is shared among nitrogen, carbon, oxygen and hydrogen in standard ultimate analysis (Durogbitan, 2019). Nitrogen, Hydrogen, Sulfur and Carbon (NHSC) are the elemental composition of the solid waste which was carried out at the laboratory in accordance with the procedures of the Association of Official Analytical Chemists (2000). The composition of waste was determined using wet oxidation. 1.0-g of the particle sample was weighed into the digestion tube and 5W of digestion mixture was added to it. The mixture was left overnight in the fume cupboard. Using a testator, the mixture was digested for 2 hours at 170° C and allowed to cool. Moreover, to digest the mixture vigorously, 30-ml of distilled water was added to the solution and mixed. 50-ml of distilled water was added to the solution to increase the volume of digested mixture to 80-ml. An Atomic Absorption spectrometer was used to identify the elements under analysis.

Volatile Matter Determination: The volatile matter percentage was carried out by heating the sample at a temperature of 50°C for 7 minutes using a muffle furnace. The crucible was cooled in the desiccator after it was removed from the furnace and weighed. The percentage loss of mass of the sample excluding the percentage moisture is the percentage of volatile matter (Durogbitan, 2019). This was calculated using this formula;

% Volatile matter =M2 - M3/M2 - M1 x 100 – MC (4)

Where;

M1=mass of empty crucible (g)

M2=mass of empty crucible + sample before heating (g)

M3=mass of empty crucible + sample after heating (g)

MC=percentage of moisture content

Ash Content Determination: Ash content is the non-combustible residue of the sample obtained after combustion which contains Sulfur and oxides. The process was carried out by burning the sample at a temperature of 750 °C for an hour in a muffle furnace without a lid. The sample was cooled in desiccators and weighed and the process was repeated constantly until a constant weight was attained according to (Durogbitan, 2019). This was calculated using this formula;

% of ash content = M3 - M1/M2 - M1 x 100 (5)

Where;

M1=mass of empty crucible (g)

M2=mass of empty crucible + sample before heating (g)

M3=mass of empty crucible + residue (g)

Ash content= M3 – M1

Fixed Carbon Determination: Mass of fixed carbon is determined by deducting the percentage of ash content, moisture content and volatile content from the total percentage according to (Durogbitan, 2019).

% FC=100 – % ASH – % MC - % VM (6)

Contamination Factor and Pollution Index Determination

Contamination factor (Cf,): The assessment of soil contamination can also be carried out using Cf. This index enables the assessment of soil contamination, taking into account the content of heavy metal from the surface of the soil and values of pre-industrial reference levels given by (Guan *et al.*, 2014)

Cf was calculated by the following formula:

$C_f = C_m/C_{p\_i}$. (7)

Where Cm—mean content of at least five samples of individual element (like heavy metal)

Cp-i—preindustrial reference value for the substances

Contamination factor/level determination

$C^i < 1$= low contamination

$1 \leq C^i < 3$ = moderate contamination

$3\leq C^i < 6$ = considerate contamination

$C^i \geq 6$ = very high contamination

Single Pollution Index (PI)

An index that can be used to determine which heavy metal represents the highest threat for a soil environment is the Single Pollution Index (PI). This is also necessary for the calculations of some of complex indices called Pollution Load Index (PLI)

Pollution load index was calculated using this formula described below according to Varol (2011);

PI = Cn/GB (8)

Where

Cn—the content of heavy metal in soil and

GB—values of the geochemical background.

PLI = $\sqrt[n]{(CF1xCF2xCF3x\ldots xCFn)}$ (9)

Where, CF = contamination factor,

n = number of metals

C metal = metal concentration in polluted sediments

C Background value = background value of that metal.

The Pollution Load Index (PLI) value of >1 is polluted, whereas <1 indicates no pollution according to Harikumar *et al*., (2009).

Statistical analysis: Data collected from the laboratory analysis were subjected to descriptive statistical analysis using SPSS version 20. Results were presented in tables (mean, and standard deviation,) and charts. ANOVA and correlation analysis were used to establish its relationship and mean separation was done using Duncan multiple range tests.

Table 1: GPS Coordinate, Wind Speed, and Wind Direction of the Study Locations:

Stream water	Latitude/ Elevation	Longitude/ Elevation	Time	Windspeed /Direction
Dominic Utuk stream	N5°2’10.08’’/ 5.03613	E7°56’25.74’’/ 7.94049	8am	1m/s,4km/h-3mph / 250°(W)
Uyo village road stream	N5°2’51.726’’/ 5.04772	E7° 6’12.696’’/ 7.93686	8.20 a.m	1m/s,6km/h-4mph / 227° (SW)
Control (Ntak Inyang)	N5°4’51.174’’/ 5.08088	E7°55’50.46.638/ 7.92958	8.40 a.m	1m/s,5km/h-3mph/107° (E)

RESULTS/FINDINGS

Determination of chemical characteristic of Whole microplastic resin in Uyo metropolis

Microplastics Ultimate assay in the surface stream water of Uyo metropolis

The chemical properties of the microplastics analyzed in the water showed that surface stream water along Dominic Utuk avenue recorded the highest concentration of Carbon (12.67%), followed by stream surface water at Uyo village road (8.78%) while the least concentration (3.22%) was observed in a control (stream water at Ntak Inyang) (fig. 2). At the same time, Dominic Utuk avenue surface stream water recorded the highest concentration of Oxygen (38.89%), followed by Uyo village road stream water (21.67%) and control recorded the least concentration (12.05%). Nitrogen content in the water recorded highest in Dominic Utuk surface stream (0.38%), followed by Uyo village road (0.15%) while the least concentration was recorded in the control sample (0.05%). Hydrogen content in Dominic Utuk avenue stream water recorded highest (7.86%), followed by Uyo village road stream water (5.18%) and control sample (2.45%). Moreover, in figure 2, Dominic Utuk Avenue recorded highest Sulphur content (0.16%), followed by Uyo Village road stream (0.11%), whereas the least was recorded in a control sample (0.03%) collected from Ntak Inyang stream.

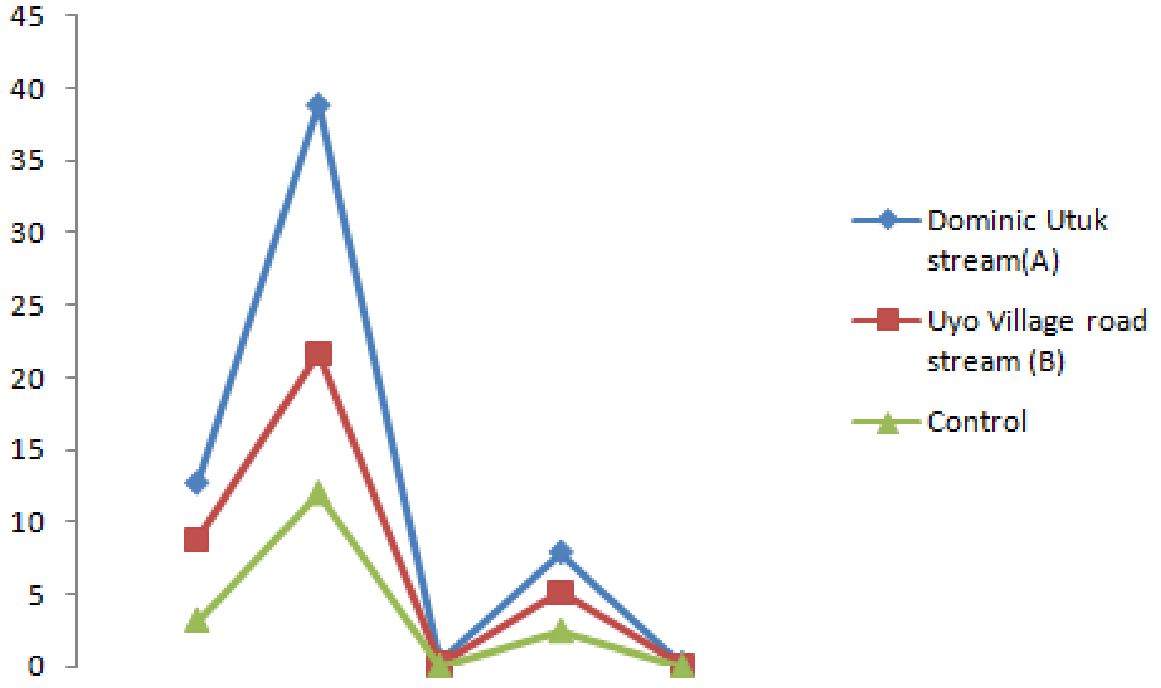

Figure 2: A line graph of the ultimate analysis of water samples of stream surface water in Uyo metropolis, Akwa Ibom State

Correlation analysis results of the relationship between the chemical characteristics of the whole microplastics in water samples collected from Uyo metropolis.

Correlation analysis was used to measure the extent of the relationship between the concentration of ultimate assay of microplastics in samples of surface water collected from Uyo metropolis in Akwa Ibom State (Table 2).

The result of the correlation analysis of the relationship between the concentration of microplastics ultimate analysis on samples of surface water collected in Uyo metropolis of Akwa Ibom state shows that some of the parameters exhibited strong correlation with each other, however these relationships are significant ($p>0.05$). According to the results reported in Tables 4.2, the correlation coefficients (R^2) between microplastic ultimate assay concentration levels at the surface water are quite very high. This is a clear indication that all pollutants have the same origin, as expected. Exceptionally, a perfect relationship between carbon-sulfur (1.000) was observed, indicating that carbon increases as sulfur increases and vice versa. Similarly, there was a strong correlation between oxygen-nitrogen (0.998) and was significant at 5% probability.

Proximate assay of whole microplastic particles in Uyo metropolis stream surface water

Dominic Utuk stream recorded the highest fixed carbon (19.85 %) content in the water of Uyo metropolis (fig 3), followed by Uyo village road stream (15.77 %) and the least was recorded in control (4.23 %). However, Uyo village road stream recorded the highest content

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of Ash in the water, followed by Dominic Utuk avenue stream (1.03 %), and whereas, the least was recorded in control samples collected at Ntak inyang stream. Concomitantly, volatile matter content of the water recorded highest in Uyo village road stream, followed by Dominic Utuk avenue stream (79.12 %) and the least was recorded in the control sample. In figure 2, the highest residual content of microplastic in water was recorded in Dominic Utuk avenue stream, followed by Uyo village road stream (0.71 %) and the list was recorded in the control sample from Ntak Inyang stream.

Table 2: Correlation analysis result of the relationship between the ultimate assay in samples of stream surface water collected from Uyo metropolis, Akwa Ibom State

CORRELATION	% C	% O	% N	% H	% S
% C	1				
% O	0.965	1			
% N	0.948	0.998*	1		
% H	0.995	0.986	0.974	1	
% S	1.000*	0.957	0.937	0.992	1

**Correlation is significant at 0.05 percent*

Table 3: Correlation analysis result of the relationship between the Whole Microplastics proximate assays of sampled surface water collected from Akwa Ibom State

CORRELATION	%Fixed Carbon	% Ash	%Volatile matter	%Residual content
%Fixed Carbon	1			
% Ash	0.681	1		
%Volatile matter	0.957	0.865	1	
%Residual content	0.999*	0.649	0.943	1

**Correlation is significant at 0.05 percent*

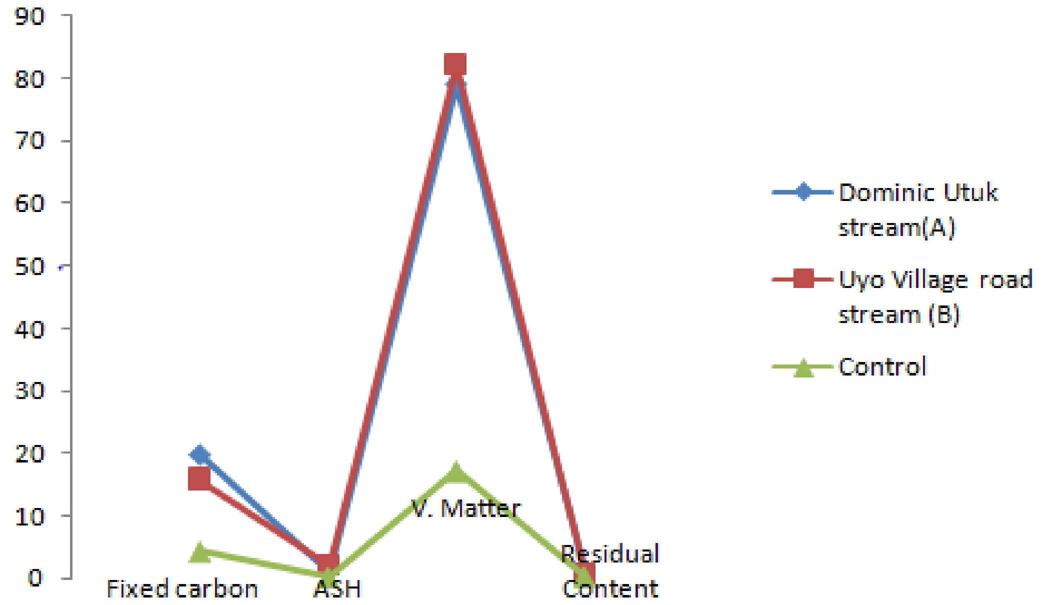

Figure 3: A line graph of the proximate analysis of stream surface water samples in Uyo metropolis, Akwa Ibom State

Correlation analysis was employed to measure the extent of the relationship between the concentration of proximate assay of microplastics in samples of surface water collected from Uyo metropolis in Akwa Ibom State and the result of the analysis is presented in Table 3.

The result of the correlation analysis of the relationship between the concentrations of proximate assay parameters on samples of surface water collected in Uyo metropolis of Akwa Ibom state shows that most of the proximate analysis parameters exhibited a strong correlation with each other. However, some of these relationships were significant ($P \leq 0.05$) while others were not significant ($P \geq 0.05$). According to the results reported in Tables 3, the correlation coefficients (R^2) between the parameters concentration levels at the surface water are quite very high. This is a clear indication that all the parameters have the same origin. However, these results showed that there was a strong correlation coefficient between Fixed Carbon-Residual content were significant at 5% level, indicating strong positive correlations. This implies that as fixed carbon increases, residual content increases and vice versa. Others that were not significantly fixed carbon-ash (0.681), fixed carbon-volatile matter (0.957), Ash-volatile matter (0.865), ash-residual content (0.649) and volatile matter-residual content (0.943) show that the level of their occurrence was not as a result of other parameters but as a result of their sources.

Determination of physical characteristic of Whole microplastic resin in Uyo metropolis

From figure 4, Uyo village road stream recorded the highest high heat value (14860KJ/g) followed by Control sample (7320.00 KJ/g) and the least was recorded in the Dominic Utuk stream (2134.00 KJ/g). However, Dominic Utuk stream recorded the highest moisture content (24.87 %), followed by Uyo village (26.72 %) whereas the least was recorded in the control sample (13.45 5). Moreover, the pH level of the resin recorded the highest value of 6.53 in

Uyo village road stream followed by Dominic Utuk road stream (6.34) and control sample recorded the least (2.43).

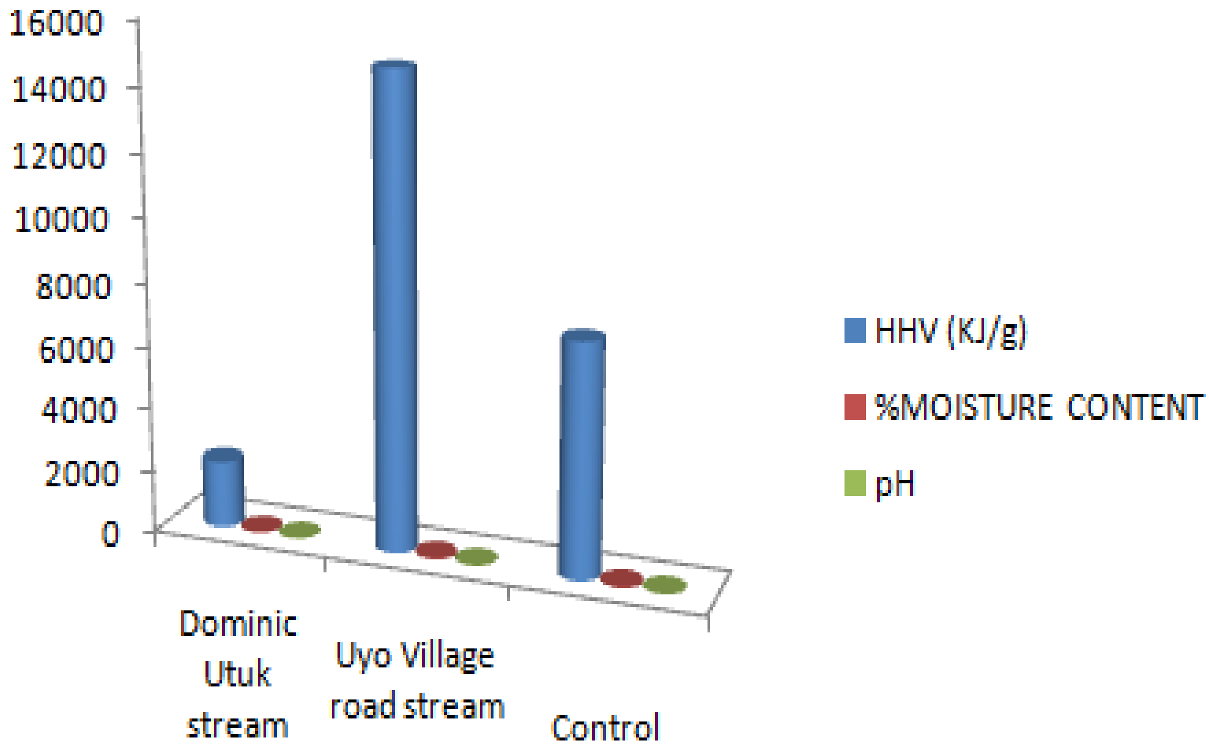

Figure 4, showing physical parameters assessed from surface stream water microplastic resin.

Correlation analysis was employed to measure the extent of the relationship between the concentration of proximate assay of microplastics in samples of surface water collected from Uyo metropolis in Akwa Ibom State (Table 4).

The result of the correlation analysis of the relationship between the concentration of physical characteristics of the microplastics on samples of surface water collected from Uyo metropolis in Akwa Ibom state shows that the parameters assessed exhibited strong correlation with each other, however these relationships are not significant, indicating that the level of occurrences of each of High heat value. Moisture content and pH in stream surface water was not as a result of the presence of other nutrients but as a result of the various sources from which these parameters entered the stream surface water in the study area.

Table 4: Correlation analysis result of the relationship between physical characteristics of the whole microplastics in the samples of stream surface water collected from Uyo metropolis.

CORRELATION	HHV (KJ/g)	%MOISTURE CONTENT	pH
HHV (KJ/g)	1		
%MOISTURE CONTENT	0.820	1	
pH	0.908	0.996	1

Water Microplastic Heavy metal and Anion concentration

Heavy metal concentration in identified in Table 5 microplastic showed that, the value of Lead-Pb concentration (46.82±0.03 ppm) obtained in Dominic Utuk stream surface water was significantly ($P<0.05$) higher than the values obtained for Uyo village road surface water (29.94±0.03 ppm) and Control site surface water (13.89±0.03 ppm), while the values obtained for Uyo village road surface water (29.94±0.03 ppm) was significantly ($P<0.05$) higher than Control (13.89±0.03 ppm).

Also, Cadmium- Cd concentration in Dominic Utuk stream surface water (6.79±0.04 ppm) was significantly ($P<0.05$) higher than the values obtained for Uyo village road surface water (3.85±0.03 ppm) and Control (1.03±0.05 ppm), while the values obtained for Uyo village road surface water (3.85±0.03 ppm) was significantly ($P<0.05$) higher than control (1.03±0.05 ppm).

Correspondingly, the Mercury-Hg^{+} value obtained from Dominic Utuk stream surface water (0.67±0.04 ppm) was significantly ($P<0.05$) higher than the values obtained for Uyo village road surface water (0.29±0.05 ppm) and Control site surface water (0.12±0.01 ppm), while the values obtained for Uyo village road surface water (0.29±0.05 ppm) was significantly ($P<0.05$) higher than Control (0.12±0.01 ppm).

Moreover, the value of Chromium-Cr obtained from Dominic Utuk stream water (39.86±0.04 ppm) was significantly higher than Uyo village road (21.18±0.04 ppm) and the control (3.02±0.08 ppm). While Uyo village road value (21.18±0.04 ppm) was significantly higher than the control site (3.02±0.08 ppm).

Arsenic-As concentration obtained from Dominic Utuk stream surface water (0.95±0.02 ppm) was significantly ($P<0.05$) higher than the values obtained for Uyo village road surface water (0.62±0.03 ppm) and Control (0.22±0.05 ppm), while the values obtained for Uyo village road surface water (0.62±0.03 ppm) was significantly ($P<0.05$) higher than Control (0.22±0.05 ppm).

Concomitantly, Anion content in Table 5 shows that Chlorine-Cl^{+} concentration obtained from Dominic Utuk stream surface water (178.59±0.03 ppm) was significantly ($P<0.05$) higher than the values obtained for Uyo village road surface water (124.86±0.05 ppm) and Control site (11.09±0.21 ppm), while the values obtained for Uyo village road surface water

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(124.86±0.05 ppm) was significantly ($P<0.05$) higher than Control site water (11.09±0.21 ppm).

Bromine-Br concentration (114.65±0.02 ppm) obtained in Dominic Utuk stream water was significantly ($P<0.05$) higher than that of Uyo village road surface water (92.35±0.03 ppm) and Control site water (13.89±0.01 ppm), whereas the concentration values obtained from Uyo village road surface water (92.35±0.03 ppm) was significantly ($P<0.05$) higher than Control site (13.89±0.01 ppm). These imply that the concentrations of the parameters in each of the locations are not significantly the same

Table 5: Mean Standard deviation of selected heavy metal and anions in the Whole Microplastics particle identified in stream water sample.

Parameters (ppm)	**SAMPLE LOCATION**			
	Dominic Utuk stream	Uyo Village road stream	Control	WHO
Pb	46.82^{a}±0.03	29.94^{b}±0.03	13.89^{c}±0.03	0.010
Cd	6.79^{a}±0.04	3.85^{b}±0.03	1.03^{c}±0.05	0.003
Hg	0.67^{a}±0.04	0.29^{b}±0.05	0.12^{e}±0.01	0.010
Cr	39.86^{a}±0.04	21.18^{b}±0.04	3.02^{c}±0.08	0.05
As	0.95^{a}±0.02	0.62^{b}±0.03	0.22^{e}±0.05	0.05
ANION CONTENT				
Cl	178.59^{a}±0.03	124.86^{b}±0.05	11.09^{c}±0.21	0.2
Br	114.65a±0.02	92.35^{b}±0.03	13.89^{c}±0.01	6.0

Values are mean ± standard deviation. The mean value in each row followed by different superscripts is statistically different at ($P < 0.05$). a,b,c -Mean separation using Duncan multiple range test.

Table 6: Correlation analysis result of the relationship between the heavy metals of whole microplastics in the samples of stream surface water collected from Uyo metropolis, Akwa Ibom State

CORRELATION	Pb	Cd	Hg	Cr	As	Cl	Br
Pb	1						
Cd	1.00**	1					
Hg	0.980	0.979	1				
Cr	1.00**	1.00**	0.978	1			
As	0.998*	0.998	0.963	0.998	1		
Cl	0.976	0.997	0.913	0.978	0.989	1	
Br	0.947	0.948	0.864	0.949	0.967	0.994	1

**Correlation is significant at 0.05 percent*

Table 7: Contamination factors (CFs) and Pollution load index of heavy metals and anions in the whole microplastics in water samples collected in AKS.

Parameters (ppm)	**Sample Locations**		
	Dominic stream	**Utuk**	**Uyo Village road stream**
Pb	3.37		2.16
Cd	6.59		3.74
Hg	5.58		2.42
Cr	3.02		7.01
As	4.32		2.82
Contamination degree	22.88		18.15
Pollution Load Index (PLI)	201.044		98.293
ANIONS CONC.			
Cl	16.10		11.26
Br	8.25		6.65
Pollution Load Index (PLI)	23.050		17.31
Contamination degree	24.35		17.91

Correlation analysis result as presented in Table 6 showed the relationship between the concentration of heavy metal of microplastic polymer on samples of stream surface water collected from Uyo metropolis in Akwa Ibom state shows that some of the heavy metal element exhibited a perfect correlation with other and were significant at 5% probability level while other heavy metal element also shows strong correlation with each other because they were close to 1, however these relationships were not significant, indicating that the level of occurrences of each of heavy metal element in the water samples of stream was not as a result of the presence of other heavy metals or the reactivity between these heavy metals but as a result of the sources from where these heavy metals enters the water bodies in the study area. According to the result reported in Table 6, the correlation coefficients (R^2) between heavy metals concentration levels at the surface water that were highly perfect are Lead-Cadmium relationship (1.00), Lead-Chromium (1.00), Cadmium-Chromium (1.00), while strong relationship was observed for Lead-Arsenic (0.998) and they were all significant at 0.05 % mean as one element increase, the other element increases too. Other relationships exhibit strong correlation relationships but were not significant indicating that their source of origin are the same as expected.

Contamination factors (CFs) and Pollution load index of heavy metals and anions

Table 7 shows the contamination factor/pollution index and pollution load index of heavy metal and anions pollutant in stream water samples in Uyo metropolis. Pollution severity and its variation along the sites were determined with the use of pollution index. Heavy metal contamination factor in Dominic Utuk stream ranges between 3.37 – 6.59 ppm with the overall degree of contamination level (22.88ppm) and pollution load index of 201.044ppm. Uyo village road stream recorded heavy metal contamination factor which ranges from 2.16 – 7.01 ppm with 18.15 ppm degree of contamination and pollution load index of 98.293 ppm. However, anion contamination factor in Table 7 shows that chlorine is recorded highest (16.10 ppm) while bromine recorded the lowest (8.25 ppm) in Dominic Utuk stream with degree of contamination (24.35 ppm) and pollution load index of 23.050. Uyo village road stream recorded Cl contamination factor (11.26) as highest while bromine recorded the lowest (6.65 ppm). The overall degree of contamination is17.91 ppm and pollution load index (17.31 ppm)

DISCUSSIONS

The research study reveals the present concentration of microplastic particles (chemical and physical properties) in the selected stream locations within Uyo metropolis of Akwa Ibom State. Proximate and ultimate components of the microplastic representing physical and chemical properties showed that ultimate properties of the particle Carbon, Oxygen, Hydrogen, Nitrogen, Sulfur, in Dominic Utuk and uyo village road water course were higher in concentration compared to the control site which was 500 meters away from the town. High concentration entails great impact on the water quality. This may be attributed to the chemical component used in the manufacturing process of plastic or microplastics. However, these plastic particles get to the water and sometimes clog the water bank/ shores thereby attracting or absorbing chemical substances from the atmosphere. Though this microplastic takes time to disintegrate in the water but with the help of these atmospheric chemicals, this helps in fastening up the breakdown process. During this process, the object sometimes can absorb more elements like hydrogen, oxygen, sulfur from the water surface which may contribute to higher concentration on its surface area. Correlation analysis between the elements showed that the element exhibited strong and positive correlation between each other and some relationships were perfectly correlated. The likes of carbon and sulfur relationship which showed that that as one increases the other follows the same trend.

Proximate assay also reveals that fixed carbon, ash content, volatile matter, and residual contents were higher in the two studied waters when compared to the control. This shows a significant increase in the study object, this means that there is a huge impact on the water body by indiscriminate waste disposal and may render the water unsafe for consumption. Thomas (1992) stated that ash content shows a great influence by the heating value of the microplastic. The ash content represents the part of the microplastics that will not combust (Thomas, 1992). This content can be influenced by the high heating capability of the microplastic recorded in the result. High heating values of the microplastic can yield high ash content, when there is low moisture content and volatile matter.

Elements like fixed carbon which recorded (19.85, 15.77 %) from Uyo village road and Dominic Utuk stream respectively and 4.23% from the control site showed that there is a high amount of carbon in it and this correlates with the high Carbon content in ultimate assay. The concentration of moisture content of the microplastics in the studied samples can be attributed to the deposition of this microparticle of this plastic over time, some surfaces may absorb water and other soluble agent some will not therefore the moisture content may affected the caloric value of the plastic although, this is in contrary.

Correlation analysis also shows that they exhibited strong correlation with each other and correlation coefficients were very high. Though some relationships were not significant at ($P \leq 0.05$) but positive relationships indicate that they are from the same source.

Physical parameters such as High heating value (14860Kj/g) from Uyo village road stream was higher than the control (7320.00kg/j) showing high presence of plastic material in the water which can be used to generate another source of energy. There was a variation from one of the study sites which has a lower high heating value of microplastic than the control. These differences could be attributed to either the flowing current of the stream of the type of thermoset present in the water. However, moisture content and pH level of the microplastic did not follow the trend rather they were all of high amount in the studied stream when compared to the control stream water. Since the microplastic particle was from the water, the high moisture content and pH level (6.53) (acid in nature) could be as a result of absorption of moisture from the water and other acidic chemicals from the atmosphere. Correlation analysis showed not a significant relationship but they exhibited a positive, strong correlation. This implies that the presence of one parameter cannot influence the increase of another parameter.

Heavy metal such as lead, cadmium, mercury, chromium, and arsenic as represented in Table 5 in both Dominic Utuk stream and Uyo village road stream were of high concentration more than the control stream site and also higher than the permissible limit by WHO. The presence of these elements could be attributed to the additive used during the manufacturing process and is in tandem with (Rochman, 2018) that heavy metals such as lead, cadmium and tin are used in the manufacturing process which includes other things like catalysts, fillers, and coloring agents, and can pose severe health risk to living organism. Similarly, anion content (Chlorine and Bromine) from the two stream waters were higher than the control. The high concentration of this chemicals poses danger to human health and it agrees with the findings of (Tanaka, *et al*., 2013; Gallo, *et al*.,2018; Teuten, *et al*., 2009) that some additive substances applied in manufacturing process of plastic, especially persistent organic pollutants (POPs) which include brominated flame retardants and polychlorinated biphenyls (PCBs), accumulate inside the tissue of organism(animals) and can transfer through the food web to cause ailment. Also these chemical element recorded in the study can be linked to the absorption process by the microplastic surface area, this agrees with (Teuten, *et al*., 2009) in his work that, many pollutants like persistent organic pollutants (POPs) and heavy metals can also adsorb or 'stick' to plastic surfaces for long time, as a result, this plastics particles (microplastics) can act in form of a sponges in the environment, passively collecting chemicals onto their surfaces area and possible absorbing them (Andrady,2011) also reported that microplastics possessed a high surface area, giving way to many potential sites for chemicals to bind and making them very good at concentrating chemical contaminants.

Therefore, these chemicals create major impacts on the water quality and may render it unsafe for consumption. From the correlation point of view, the metals and anions exhibited strong positive and perfect correlation with each other. Other relationships exhibit a strong correlation but were not significant indicating that their sources are the same as expected as seen in Table 6.

Moreover, from the contamination factor and pollution index analysis, these elements are dangerous to the living organism consuming the water because they are higher in the two streams compared to the control. The heavy metal and anions recorded in the stream surface water as a result of additives in the plastic manufacturing process and packaging of toxic chemicals like car battery breakdown and are discharged to the waterways through runoff.

IMPLICATION TO RESEARCH AND PRACTICE

Survey of microplastic particle chemical and physical parameters in the water of Uyo metropolis showed a positive implication to research because it has revealed the bad actions of humans to the environment as a result of indiscriminate waste disposal. The parameters assessed put more light on the effect of the high present of microplastic in the environment. It therefore opens more gaps on the research problems which need to be done in order to assess the types of this polymer, the chemical composition and toxic chemicals attached to it. The findings of this study proved that there is presence of microplastic in the stream water present within the study area and proper monitoring should be done in order not to flow or move to other locations. This will help regulate the usage and disposal in our environment.

CONCLUSION

Microplastic pollution causes harm to the communities and industries that use water from the streams to support their livelihoods especially through contamination; damaging of aesthetic view and intrinsic value and so on. The findings from this study conclude that, water ways, water course of the Uyo metropolis is clogged with a high amount of microplastics especially along the banks which are not physically seen at the distance. The analyzed microplastic ultimate and proximate properties were higher compared to the control stream away from the metropolis. This high amount can be attributed to the indiscriminate usage and disposal of single use plastic in the area. And since it is an urban area full of many economic and social activities, the presence of the microplastic substances may be linked to population growth and urbanization. High calorific energy (high heating value) of the microplastic can be converted to usable energy through recycling process and proper thermal treatment operation is important to control emissions of these compounds. This could help reduce the quantity of plastics disposed of. Heavy metal and anions concentration found in the microplastic are dangerous to the aquatic species and could also affect the food web.

Future Research

Study findings recommend proper research on recycling, reuse of plastic materials rather than disposal. Thermal treatment technology such as refuse derived fuel (RDF), power plant or thermal depolymerization is recommended since the microplastic particles have high heating value for energy conversion. The researcher also recommends that there should be more and intensified legislation on the reduction of plastic usage and disposal to the environment. Government should ensure plastic sorting from other debris when disposing or filling it.

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