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Key Words Polycyclic aromatic hydrocarbons, water, Acenanphthene fluorine Effect of climate change on water on urban dwellers in Warri metropolis ¹Gbodo, E.A and ²Onuoha, T

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Abstract

Climate change also known as climate emergence is a major environmental problem of concern all over the world. The impact of climate change on the activities of urban dwellers in Warri has been studied. The study was aimed at determining the concentration of polycyclic aromatic hydrocarbons in water. The estimated acceptable daily intake for adults and children of these pollutants was also determined. Standard analytical methods for determining PAHs was employed according to United states environmental protection agency (US EPA) and World health organization (WHO). The results showed levels of chromatogram and mean concentration of sixteen (16) PAHs in water analyzed. It was observed that Acenanphthene and fluorine were the two PAHs in water sample with the range of 1.49 and 0.96ppm respectively. However, health impact assessment of treated water should be carried out to identify the hazards and risk factors that may be associated with PAHs in water. The current study established that the levels of Acenanphthene (Ace), acenaphthylene (Act) in borehole water were below the limits set by WHO, US EPA, WB and NEMA. The public health concern in terms of borehole water in warri south, south part of Nigeria industrial area of the country is therefore paramount to be monitored regularly as such level will bioaccumulate in these samples assessed with time and pose public threat.

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Introduction

Climate change also known as climate emergence is a major environmental problem of concern all over the world. The US geological survey sees climate change as the increasing changes in the measure of climate over along period of time including precipitation, temperature and wind pattern increasing concentration of greenhouse gases in the atmosphere and the side effect of warming - like melting glacier, heavier rainstorms or more frequent drought. The activities of human like burning of fossil fuels like coal, oil (Hydrocarbons)-and gas releases CO2, sulphur and its oxides and polycyclic hydrocarbons to the underground water (Adishi and Oluka, 2018).

Today, human are the ones causing CO2 level to increase in the atmosphere by taking ancient carbon from geological deposits of fossil fuels and putting it into the atmosphere by burning. Since 1750, carbon dioxide concentration has increased by almost 50 percent. Methane and nitrous oxide, chloroflorocarbon (CFC) and other important anthropogenic greenhouse gases that are released mainly affect underground water reservoirs over the last 250 years (Anyika,2020).

The greenhouse effect of these radioactive gases on the earth atmosphere is rising temperature of the atmosphere, a phenomenon known as globalwarming. The rate of warming in the past 30years exceed any comparable period in the entire measured temperature record (NASAscientist.) Significant climate change has occurred on earth in the past, and most certainly in the future because of the long term influences that cycle earth through swings from ice age to warmer periods (Ayinde et al., 2020). For instance, heatwaves have always happened but they are shattered records in recent years. In June 2020, a town in Siberia registered temperature of 100 degrees. In Australia, meteorologist have added a new color to their weather map to show areas where temperature exceed 125 degrees. Rising sea level have also increased the risk of flooding in diverse places because of storm surges and high tides (Berhanuand Wolde, 2019).

The consequences of climate change due to human activities has affected the planet entire ecosystem which hasked to acidification and deoxygenation in some developed countries like United States of America and India. In Nigeria, May, Volume 10, Number 2, Pages 159 - 164 https://doi.org/10.5555/IYGL7896

especially in Niger delta area there has been an increaseintemperaturewhich hasledtorise in sea level and caused alot of ecological challenges of ocean acidification, deoxygenation, change inbiodiversity, water unfit for consumption, low agricultural output due to soil contamination, release of polyclic hydrocarbons and a threat to end consumers. Therefore, the need to carryout investigation to curb the menace which has infflicted great pain and suffering to the inhabitants in Niger delta(Warri) metropolis and Nigeria at large. This research was aimed to determine the effect of climate change in water on urban dwellers in Warri metropolis.

Materials and Methods Sample Collection

Random sampling of water samples were collected from shell ramp area of warri metropolis and control sample were collected from rural area of Udu community where human activities like burning of hydrocarbonis low. Samples were sent to analytical laboratory for analysishe Study Area

Warri is the headquarter of Warri south local government area Delta State Nigeria. It is situated at about 50km from the coast of the lower Niger Delta of Delta State. It lies along the Warri river navigable channel at about the intersection of longitude $5^{\circ} 45^{I}$ east and latitude $5^{\circ}3^{1}$ north of the equator. Warri is built where the wide stretch of the mangrove swamp occurs in the Niger delta. It is located at the landward edge of the mangrove swamp. The swamps are boarded on the landward side by firm sedimentary rock of the coastal plain formation (Udo, 1970). Warri is lowly in generally about 100 to 350cm above sea level. The soils are generally muddy, sandy and clayey providing an unsuitable for road and buiding construction works (odemerho, 1988).

The vegetation varies from the mangrove swamp along the coast to evergreen forest in the hinterland. Warri and its environs are straddled by many creeks, swamps, rivers, meanders and estuaries thus exhibiting poor drainage and a difficult terrain a characteristics of Niger delta region. Warri, most times is regarded as noman'sland. This is because it has attracted people from all over the world. This is because of her status as a major industrial town in Nigeria. The major ethnic groups in Warri are the Itsekiri, Urhobos and the Ijaws. In 1952, the population of Warri was put at 19,525. In 1963, it was 55,256. Estimates indicates that the population had reach 130,000 in 1971 (Makinwa, 1978). The current population of Warri is put http://www.ijbst.fuotuoke.edu.ng/ 160 ISSN 2488-8648

at 217,504 (provisional census report 1991) and 248, 026 as projected figure for 1996.

GC Analysis for the Determination of Polycyclic Aromatic Hydrocarbons (PAHS) in Water Samples

Reagents: PAHs mix standards containing sixteen mentioned PAHs were obtained from Supelco Company (Bellefonte, PA, USA). In dichloromethane, the standard solutions were ready, with all of 16 PAHs (0.1 mg/mL). After that, these stock standard solutions with dichloromethane-methanol (50:50, v/v) were diluted every week to make a solution of working mixed (1 mg/mL for each PAH) that it was applied to determine extraction function with variant situations. For internal standard (I.S.) biphenyl, was used (0.05 ug/mL in methanol). Working and stock solutions were preserved at four centigrade degree. MWCNT were bought from Hanwha nanotech Company (MWCNT CM-95, Korea). Similar to the past research, MWCNT-MNP (as adsorbent) was ready (Ikem, 2018). Finally, all extra solvents and chemicals were of grade of analytical-reagent. Sample preparation

Five grams of each soil and crushed samples of dried pumpkin and five milimiter of water, weighed and transferred to 50 mL conical tube. Then, added 1 mL of the internal standard to the samples. Afterward, the sample was homogeneous, and after adding 7.5 mL of 1 M potassium hydroxide and 7.5 mL of 30%v/v methanol-acetonitrile, homogenization was performed on a shaker with 300 rounds for 5 min. The samples were placed in ultrasonic baths of German model Alma, at a temperature of 40-45 °C for 15-30 min at a frequency of 130 Hz. After removing the conical tubes from the ultrasonic bath and their temperature reaches the ambient temperature, for separation of the fat phase, the samples for half an hour were centrifuged at 4500 rpm. The supernatant was then slowly moved to a 100 mL Erlenmeyer flask. The pH was measured by a pH meter. To adjust the pH to 6.5–7, because the initial pH of the samples was 13, a few drops of concentrated hydrochloric acid (about 6 drops) were added to the samples to reduce pH 9-10, then with hydrochloric acid (1 M), slowly adjusted to pH 6.5–7.

After primary clean up, for adsorption of analytes, 10 mg of magnetic nanocarbon adsorbent and 500 mg of NaCl were added to the samples and then homogenized with a shaker for 10 min. The samples were then transferred to the incubator at 40–45 °C for 12–24 h. The last step involves separating the analytes from the absorbent, which, after the relative drying of the samples, add 5 mL of dichloromethane as solvent

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to the specimens. It was then homogenized with a shaker at 300 rpm for 10 min. Then, by a magnet (external), the non-impure fluid was slowly moved to the vials. The samples are then sealed, covered with aluminum, and stored at -18 °C until they are sent to the laboratory and injected into the GC–MC device to prevent light from entering.

Analytical Conditions and Instrumental

The examination was done on a device of Agilent GC 6890 with a detector of MS 5973 quadrupole (Technologies of Agilent, Palo Alto, CA, USA). It was regulated with a column of capillary of DB-5 ms (30 m, 0.25 mm i.d., 0.25 µm thickness of film). For inlet, the mode was splitless. The temperatures were regulated as follows: the primary temperature of oven 70° (on the Celsius scale), the temperature of injector 290° (on the Celsius scale); retained for 1 min, at a rate of 10° (on the Celsius scale) /min raised temperature to 295° (on the Celsius scale), retained for 7 minutes. The temperature of transfer line was retained at 300° (on the Celsius scale). For carrier gas, helium (He) with constant flow was used (1 mL/min). The temperature of quadrupole was retained at 150° (on the Celsius scale) and temperatures of source were kept at 230° (on the Celsius scale). At 70 eV, the energy of electronic beam of the MS was regulated. The qualification was done by comparing the achieved mass spectra and times of retention to reference spectra. By injection calibration standards in same GC/MS conditions, the times of retention were obtained. With using SIM mode, the PAH analytes were quantified.

Human health risk assessment of water consumption

To estimate the carcinogenic risk of detected heavy metals and PAHs to humans, using two population

Results

Table 1: Mean concentration of Polycyclic Aromatic Hydrocarbon

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groups(young children and adults) the estimated acceptable daily intake (EADI) was used. EADI was obtained by multiplying the residual water concentration (ug/kg) by the consumption rate in Nigeria (L/day orkg/day) and dividing the product by the body weight (kg)(Fianko*et al.*, 2011). The hazard quotient (HQ) was then obtained from the ratio of EADI and reference dose. The reference dose (RFD) of each heavy is the exposure that is likely to be without an appreciable risk or deleterious effects and was provided by the USFDA (1999).The food and agricultural organization (FDA,1999) quotes the per capita consumption of water in Nigeria as 9 kg. The following formula was used to estimate the dietary intake.

EADI =C x CR/BW(Fianko et al., 2011).

EADI is the estimated average daily intake, C is the concentration of PAHs, CR represents consumption rate of water while BW represents the body weight of age group. The food and agricultural organization (FDA,1999) quotes the per capita consumption of ready to eat vegetable in Nigeria as 9 kg.,while body weight was set at 70 kg for adult population group.

Hazard quotient (HQ): Hazards quotients were obtained by dividing the EADI by their corresponding reference dose (RfD).

Hazard quotient (HQ) =EADI/RfD(Fiankoet al., 2011).

Hazard index (HI): using the hazard quotient equation above, the hazard index (HI) was obtained. Hazard index is used to assess the risk involved in exposure to mixtures of the detected PAHs and heavy metals. Hazard Index(HI)= $\sum_{i}^{n} HQl$.(Fianko *et al.*, 2011).

Compound	R.T.QIon	Response		Conc Units Dev(Min))
Target Compounds					
1) Naphthalene	0.000		0	N.D.	
2) Acenaphthylene	0.000		0	N.D.	
3) Acenanphthene	10.301	153	151770	1.49 ppm	76
4) Fluorene	10.299	166	58136	0.96 ppm	1
5) Phenanthrene	0.000		0	N.D.	
6) Anthracene	0.000		0	N.D.	
7) Fluoranthene	0.000		0	N.D.	
8) Pyrene	0.000		0	N.D.	

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9) Chrysene	0.000		0	N.D.		
10) Benz(a)anthracene	0.000		0	N.D.		
11) Benzo(b)fluoranthene	0.000		0	N.D.		
12) Benzo(k)fluoranthene	13.784	252	42381	0.05 ppm	1	
13) Benzo(a)pyrene	13.784	252	42381	0.05 ppm	1	
14) indeno(1,2,3-cd)pyrene	0.000		0	N.D.		
15) Dibenz(a,h)anthracene	0.000		0	N.D.		
16) Benzo(g,h,i)perylene	0.000		0	N.D.		

Key: ND = Not determined (m) = manual integration ppm = parts per million PAHs=Polycyclic aromatic hydrocarbons

Table 1 above represents the mean concentration results of 16 Polycyclic Aromatic Hydrocarbon of water sample and it reveals that Acenanphthene and Fluorene were the two Polycyclic Aromatic Hydrocarbons with about 1.49 and 0.96ppm at high retention time

Table II: Estimated acceptable daily intake (EADI) and hazard quotient (HQ) for PAHs in consumption of water

`PAHs	Concentration	CR	child		Adult		RQ
Act	0.02	9	EADI	HQ	EADI	HQ	
Ace	0.98		2.8E-04	1.6	3.57E-05	1.0	_
Hazard index			0.9		0.8		8.0E

Key: Act: Acenaphthylene, Ace: Acenanphthene

Table II shows the estimated acceptable daily intake of Acenanphthene (Ace) and acenaphthylene (Act) in consumption of water and pumpkin by children and

Discussion

In the 1st step, the analytical technique involved liquid extraction of PAHs and in the 2nd phase, SPE technique using a composite of MNP-sized. The extracted polycyclic aromatic hydrocarbons were then evaluated using a technique of GC-MS (sensitive instrument). The mass spectrum (full scan), toward the recognition goal, the ratios of four characteristic ions and the \pm 0.5 percent relative retention time (RRT) tolerance criteria compared to the standard was applied. For purpose of quantification, the most intense ion was applied of each compound. The compounds were quantified by SIM mode (selected ion monitoring). The dwell time (for each ion) was regulated at 100 min. To reduce the time of examination, the conditions of GC were selected while allowing all compounds (PAHs) to elute in acquisition collections include a proper number of ions for checking. For each compound were controlled two qualifier ions and one quantitation (Ayo et al., 2014). For analysis, the conditions of optimum were supplied and the calibration curves were made (0.050adults . The results revealed that Ace was more in adults with a range of 3.57 E-05 followed by Act with 2.8E-04

5.000 µg/kg) with a coefficient of correlation was 0.979–0.994. Based on the guideline of International Council for Harmonization (ICH), the limit of quantification (LOQ) for each compound, was determined (EC,2004). The conclusion of validation tests designated that limit of detection (LODs) and LOQs for the PAHs analytes altered 0.020-0.080 and 0.063–0.242 µg/kg, respectively. According to the precision of interday via analysis QC (quality control) samples, ready on three repeated days at four levels, the accuracy of the method was assessed. Other hands, for all of the PAH compounds, the precision of interday values were fewer than 8.9%. For repeatability, the estimated values were between 4.1 and 10.6 percent and the recoveries estimated between 91.2 and 101.7 percent. By all these results to measurement the PAHs in consumable water, the reliability and feasibility of the established technique were confirmed. By examining randomly collected samples, the selectivity of the technique was confirmed. At the end, no interfering peak was seen, in the area of the analytes and internal standard . The

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findings in Figure 1 and Table 1 show different levels of chromatogram and mean concentration of sixteen (16) PAHs in water analysed. It was observed that Acenanphthene and fluorine were the two PAHs in water sample with the range of 1.49 and 0.96ppm. The results in this study are in conformity with the previous results of European Commission (EC, 2004) established for maximum level(5.0ppm) of Acenanphthene and fluorine in water. Again, the results is in conformity with the previous results of Fasonsona and Omojola,(2005) that the presence of PAHs in perishable water as a result of human activities are human to consumers even if it is below the European commission maximum level(5.0ppm) (Tirado et al., 2010; Wossen et al., 2018; Uwazie, 2020). The results obtained from this study is in line with the results presented during the third United Nations Environment Assembly hosted by Kenya at UNEP headquarters (Gigiri) in December 2017, Kenya promised to improve the lives of its people by cleaning up water. Industrial, sewage and domestic wastes have been finding their way into Nairobi river in Kenya, hence making the river unsuitable for use(Tirado et al., 2010) According to UN Environment, over 80% of the world's waste water is released into the environment without treatment, polluting the fields where plants grow, lakes and rivers (Uwazie, 2020. Such pollutants like Lead(Pb) Cadmium(Cd) and Mercury(Hg) can easily flow from the environment into humans directly or indirectly. Water and soil pollution with heavy metals in developing countries emanate from poor disposal of

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industrial and urban wastes (<u>Anyika ,2020</u>). Municipal and industrial wastewater should be treated as a strategy of minimizing the contaminants. However, health impact assessment of treated water should be carried out to identify the hazards and risk factors that may be associated with pollutants inunderground water (<u>Muringai *et al.*,2020</u>). Table II shows the estimated acceptable daily intake of Acenanphthene (Ace) and acenaphthylene (Act) in consumption of water by children and adults .The results revealed that Ace was more in adults with a range of 3.57E-05 followed by Act with 2.8E-04.

The current study established that the levels of Acenanphthene (Ace), acenaphthylene (Act) in borehole water were below the limits set by WHO, US EPA, WB and NEMA. The public health concern in terms of borehole water in warri south south part of Nigeria industrial area of the country is therefore paramount to be monitored regularly as as such level will bioaccumulate in these samples assessed with time.

Conclusion

The current study established that the levels of Acenanphthene (Ace), acenaphthylene (Act) in borehole were below the limits set by WHO, US EPA, WB and NEMA. The public health concern in terms of borehole water, pumpkin in warri south south part of Nigeria industrial area of the country is therefore paramount to be monitored regularly as such level might bioaccumulate in these samples assessed with time and may cause heath issues to humans.

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