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Assessment of BTEX Concentration in Soils and Earthworm (*Aporrectodea Longa*) From Two Automobile Workshops in Benin City, Southern Nigeria

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ABSTRACT: Automobile workshops are known to be sources of release of hydrocarbons from spent engine oil and gasoline into the terrestrial environment where they may be accumulated by soil in fauna such as earthworms. These hydrocarbon wastes often contain benzene, toluene, ethylbenzene and xylene. This study was carried out to determine the concentration of benzene, toluene, ethylbenzene, and xylene (BTEX) in soil and earthworm from selected auto mechanic workshops from Isihor and Agbor Park areas in Benin City. Soil and earthworm samples were collected for three months and the samples were prepared and analysed to determine the concentrations of BTEX. The soil and earthworm extraction were carried out using the EPA 5021 Method. Some physical and chemical properties of soil were analysed using standard procedures while BTEX was analysed using Gas Chromatograph Agilent 6890 Series, with an FID detector. The results showed that only benzene was detected in the soil at the end of the study. Toluene, ethylbenzene and xylene were below detection limits probably due to volatilization. Mean concentrations for benzene throughout the study period for soil and earthworm were 9.03±4.34 and 6.10±2.95 µg/kg respectively for site A, while the mean concentrations for benzene for soil and earthworm were 13.42±5.35 and 15.02±3.44 µg/kg respectively for site B. The percentage concentration of Benzene compound analysed in the soil and earthworm was at 52% for soil while 48% was recorded for earthworms. An inverse correlation was observed between the concentration of BTEX and pH, EC, Fe, Mn, Zn, Cu, Cr, THC, clay and silt content of the soil. Currently, there are no standards/limits available for BTEX concentrations in soil and earthworm for comparison.

Keywords: BTEX, Soil, Earthworm, Environment.

Introduction

The development of human civilization throughout history has led to a growing disruption of the natural balance and the occurrence of different types of pollutant (Lutts *et al.,* 2004). The world depends on oil and the use of oil as fuel has led to intensive economic development worldwide (Abdullah *et al.,* 2004). Environmental pollution with petroleum and petrochemical products has been recognized as a significant and serious problem (Smith and Guentzel, 2010). Most components of oil are toxic to humans and wildlife in general, as it is easy to be incorporated into the food chain. This fact has increased scientific interest in examining the distribution, fate and behaviour of oil and its derivatives in the environment (Abdullah *et al.,* 2004). There are several other automobile workshops scattered all over the major cities in Nigeria from which used engine oils, lubricating oils and other solvents containing petroleum hydrocarbons are indiscriminately dumped or spilled on every available space by artisans in the business of auto-repairs. These used oils and solvents form part of the most hazardous wastes are commonly generated in auto-repair shops around cities in Nigeria (Iwegbue, 2007).
BTEX is an acronym that stands for benzene, toluene, ethylbenzene, and xylene (Baker and Eisenreich, 2000). These compounds are some of the volatile organic compounds (VOCs) found in fossil fuels derivatives such as petroleum (gasoline). Toluene, ethylbenzene, and xylenes have harmful effects on the central nervous system. BTEX are notorious due to the contamination of soil and groundwater with these compounds (Baker and Eisenreich, 2000). Contamination typically occurs near petroleum and natural gas production sites, petrol

stations, and other areas with underground storage tanks (USTs) or above-ground storage tanks (ASTs), containing gasoline or other petroleum-related products.

The main source of BTEX contamination is the leakage of gasoline from faulty and poorly maintained underground storage tanks. Other sources of BTEX contamination are releases from large bulk facilities (Lutts *et al.,* 2004), surface spills, and pipeline leaks. Once released to the environment, BTEX can volatilize (evaporate), dissolve, attach to soil particles or degrade biologically (Baumard *et al.,* 1999).

Exposure to BTEX can occur by ingestion (consuming water contaminated with BTEX), inhalation (exposure to BTEX present in the air) or absorption through the skin. Inhalation of BTEX can occur while pumping gasoline or while showering or bathing with contaminated water. Absorption of these chemicals can occur by spilling gasoline onto one's skin or by bathing in contaminated water (Baussant *et al.,* 2001a). Acute exposures to high levels of gasoline and its BTEX components have been associated with skin and sensory irritation, central nervous system depression, and effects on the respiratory system. These levels are not likely to be achievable from drinking contaminated water, but are more likely from occupational exposures. Prolonged exposure to these compounds has similar effects, as well as the kidney, liver and blood systems (Baussant *et al.,* 2001). According to the U.S. Environmental Protection Agency (U.S. EPA), there is sufficient evidence from both human and animal studies to believe that benzene is a human carcinogen. Workers exposed to high levels of benzene in occupational settings were found to have an increase incidence in leukemia (Baussant *et al.,* 2001). In the last few decades, the concentrations of BTEX in ecological and aquatic organisms have been extensively studied in different parts of the world. Most studies have addressed the concentration of heavy metals in the edible parts (Anderson *et al.,* 2004). However, other studies reported the distribution of metals in different organs like the liver, kidneys, heart, gonads, bone, digestive tract and brain. According to the literatures, BTEX bioaccumulation in soil and subsequent distribution in soil organisms is greatly inter-specific. In addition, many factors can influence BTEX uptake like sex, age, size, reproductive cycle, swimming patterns, feeding behaviour and living environment, that is their geographical location. The aim of this study is to determine the concentration of BTEX in soils and earthworms from two selected auto-mechanic workshops from Isihor and Agbor Park Area in Benin City.

Materials and methods

*Collection of samples***:** This study was carried out at two automobile mechanic workshops in Benin City (Figure 1). The study area is located on flat open land which was formerly left in a pristine state. Soil and earth worm samples were collected from two auto-mechanic workshops in the vicinity of Isihor and Agbor park area in Benin City. The soil samples were taken in clean polyethene bags for soil analysis while the earthworm samples were taken in clean plates for laboratory analysis.

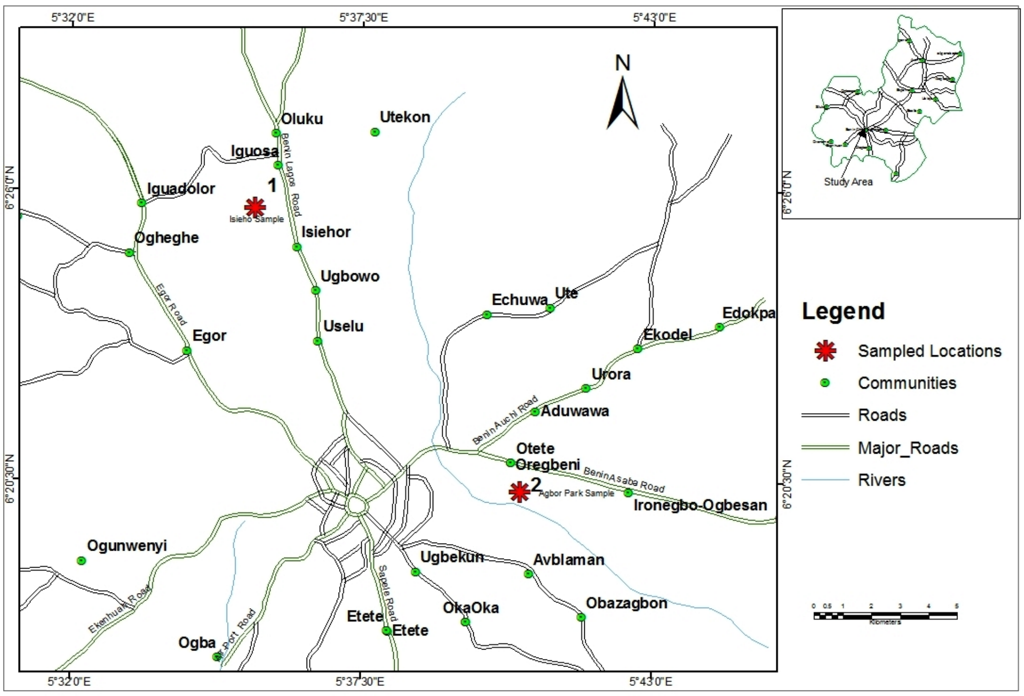

FIG. 1: MAP OF BENIN CITY SHOWING THE SAMPLED LOCATIONS

BTEX Extraction and laboratory analysis: The procedure for BTEX Extraction was according to EPA Method 5021. Five (5) grams of soil was added to 2g of anhydrous sodium sulfate ($NaSO_4$) and stirred with a stirring rod. Then 50ml of methanol was added to the sample and stirred with a magnetic stirrer for about 20 - 30mins. The extract was then ready to be cleaned up and was fractionated using silica gel Solid Phase Extraction (SPE). The same procedure was carried out for earthworm extraction.
Silica Gel Clean Ups: Glass wool was placed at the base of the syringe cartridge. Then 5g of silica gel was weighed into the cartridge. The cartridge was conditioned by rinsing with 5ml of the methanol. The methanol was allowed to flow through the column until the head of the liquid in the column was just above the column frit. The collected methanol was discarded. The extract was loaded into the column and the elutant was collected immediately in a 25ml volumetric flask. Prior to exposure of the column frit to air, the column was eluted with an additional 5ml of methanol into the column again to remove completely the little amount of BTEX present in the sample. The final extract was transferred to labeled 2ml flask auto sampler vials with Teflon-Lined rubber caps. BTEX was analysed using Gas Chromatograph Agilent 6890 Series, with an FID detector. Column dimensions was capillary 30.0m x 320µm x 0.00 µm. Detector temperature was 300ºC. Inlet temperature was 200ºC. Pressure set point was 15.0 psi and the carrier gas was helium. Oven temperature program used was 50ºC (held for 5 minutes) to 200ºC at 15ºC/min to 210ºC at 2ºC/min for 10min. The injection volume of the 2ml flask auto sampler vial was1.0 µl with a total cycle time run 19.67minutes for each sample injected. External calibration was carried out using BTEX standards. From the chromatogram, the retention times of the standards were used for the identification and quantization of the individual BTEX. All other solvents used were of high purity analytical grade.
Statistical analysis: Values have been presented as mean ± standard deviation. Data collected were subjected to Excel and SPSS using analysis of variance at $p>0.05$ significant levels.

Results and discussion

Table 1 shows the summary of BTEX concentration in the earthworms obtained from the two sites studied. Six BTEX compounds were analysed in the soil. Only benzene was found in site A and site B respectively while the other compounds were not detected probably due to the high volatilization or dissolution which may have occurred during the process of extraction. Studies have documented that earthworms have the potentials to effectively bioremediate and detoxify heavy metals through several methods such as methylation, sequestration and growth dilution (Langdon *et al.*2001).

Table 1: BTEX concentration in the earthworms obtained from two auto-mechanic workshops in the vicinity of Isihor and Agbor park area in Benin City

	Sites		
	A	**B**	
Component	**$\bar{X}$±SD**	**$\bar{X}$±SD**	**P-Value**
Benzene (µg/kg)	6.10±2.95	15.02±3.44	p<0.05
Toulene (µg/kg)	0.00±0.00	0.00±0.00	p>0.05
Ethylbenzene (µg/kg)	0.00±0.00	0.00±0.00	p>0.05
m-Xylene (µg/kg)	0.00±0.00	0.00±0.00	p>0.05
p-Xylene (µg/kg)	0.00±0.00	0.00±0.00	p>0.05
o-Xylene (µg/kg)	0.00±0.00	0.00±0.00	p>0.05
Total (µg/kg)	6.10±2.95	15.02±3.44	p<0.05

p>0.05 – No significant difference; p<0.05 – Significant Difference

The nature of activities going on in the two mechanic workshops recorded high influence on the benzene concentration in the soil. Benzene was significantly higher ($p<0.05$) in site B than site A for earthworms. The benzene concentration range from 15.02±3.44 in site B to 6.10±2.95 in site A. Ekperusi and Aigbodion (2015) reported the elimination of toluene, ethylbenzene and xylene from the contaminated soil leaving some fractions of benzene at the end of the study; this was also reported in this study. Among the BTEX component of petroleum, benzene has been reported to be recalcitrant in bioremediation process (Ekperusi and Aigbodion, 2015). This could be attributed to high human activities in the mechanic workshop at Agbor Park Area (site B)

than Isihor Area (site A). Recognisance survey during the course of this study from mechanics in the two workshops made reference to how busy they are from day to day activities and there was a much higher percentage of human activity in site B than site A either due to the human population and activities in the area.
Table 2 shows the summary of BTEX concentration in the soils obtained from the two sites. Six BTEX compounds was also analysed in the soil. Only benzene was found in site A and site B respectively as noticed with earthworm.
When compared to BTEX in soil, the result of the study recorded a high concentration of benzene in soil obtained in site B than Site A. This shows the high Benzene concentration in the soil and corresponding bioaccumulation in the tissue of earthworms living in that ecosystem. Other compounds such as Toulene, Ethylbenzene, Xylene, m, p and o-Xylene all measure in (µg/kg) was not detected due to volatilazation and degradable nature of these compounds.

Table 2: BTEX concentration in the soil samples obtained from two auto-mechanic workshops in the vicinity of Isihor and Agbor park area in Benin City

	Site A	**Site B**	
Component	**$\bar{X}$±SD**	**$\bar{X}$±SD**	**P-Value**
Benzene (µg/kg)	9.03±4.34	13.42±5.35	p>0.05
Toulene (µg/kg)	0.00±0.00	0.00±0.00	p>0.05
Ethylbenzene (µg/kg)	0.00±0.00	0.00±0.00	p>0.05
m-Xylene (µg/kg)	0.00±0.00	0.00±0.00	p>0.05
p-Xylene (µg/kg)	0.00±0.00	0.00±0.00	p>0.05
o-Xylene (µg/kg)	0.00±0.00	0.00±0.00	p>0.05
Total (µg/kg)	9.03±4.34	13.42±5.35	p>0.05

p>0.05 – No Significant Difference; p<0.05 – Significant Difference

Figure 2 shows the spatial variation of benzene concentration recording high concentration in site B than site A in both soil and earthworms. For benzene concentration in the soil, there was no significant difference between the two sites.

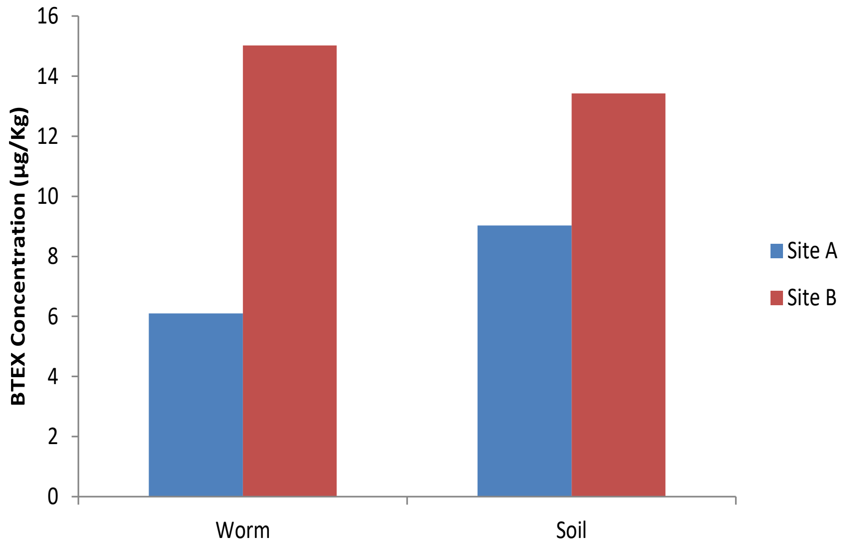

Figure 2: BTEX concentration in the earthworms and soil samples obtained from the two sites

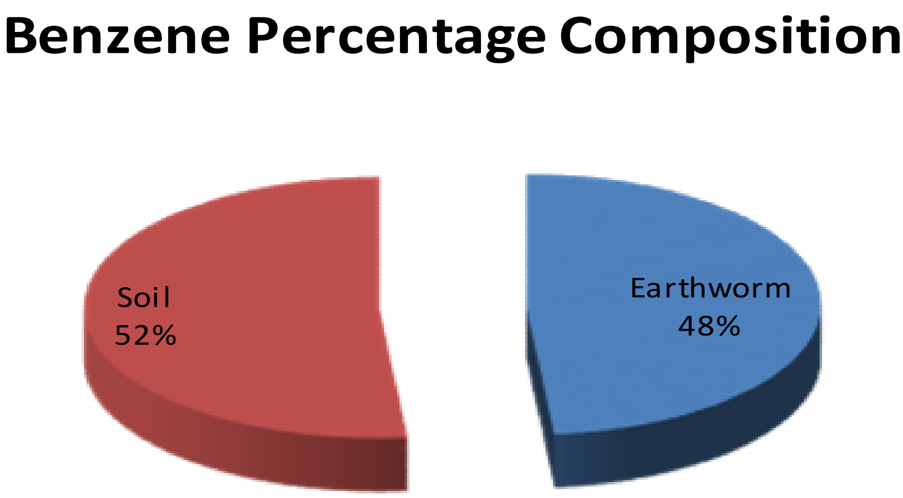

Figure 3: shows the percentage concentration of Benzene compound analysed in the soil and earthworm

From the pie chart, (figure 3), the percentage concentration of Benzene compound analysed in the soil and earthworm was at 52% for soil while 48% was recorded for earthworms. Although BTEX are known to vapourize in contaminated sites, they can remain locked in soil for months and even years as reported by the United Nations Environment Program assessment in Ogoni land (UNEP 2011), hence they need special attention in crude oil-contaminated soil. Each of these compounds or their combination poses a serious concern to human health, living organisms and the environment. Benzene is a notorious cause of bone marrow failure. Substantial quantities of epidemiologic, clinical, and laboratory data link benzene to aplastic anemia, acute leukemia, and bone marrow abnormalities (Kasper *et al*. 2004) and myelodysplastic syndrome. Human exposure to benzene is a global health problem. Animal studies have reported effects on the blood, liver, and kidneys from chronic inhalation exposure to ethylbenzene (Bayssant *et al*., 2001).

Conclusion

The concentration of BTEX was assessed in soil and earthworm from two auto mechanic workshop in Benin City. The soils analysed showed high concentrations of benzene while toluene, ethylbenzene and xylene were below detection limits. This research has shown that the earthworm (*Aporrectodea longa)* bioaccumulated benzene from crude spent oil-polluted soil. This accumulation was below the concentration determined in soil.

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