# Polycyclic Aromatic Hydrocarbons (PAHs) and Benzene, Toluene, Ethylbenzene, and Xylene (BTEX) Contamination of Soils in Automobile Mechanic Workshops in Port-Harcourt Metropolis, Rivers State, Nigeria.

Osu Charles .I<sup>1</sup>, Asuoha, Adaku N.<sup>2</sup>

<sup>1</sup>Department of Pure and Industrial Chemistry, University of Port Harcourt, P.M.B 5323 Choba, Port Harcourt,

Rivers State, Nigeria.

Telephone: +234 803 7783246 email: <u>charsike@yahoo.com</u>

<sup>2</sup>Safety Health and Environmental Department, Mobil Producing Nigeria

**Abstract:** Soil samples from automobile mechanic workshops in Port-Harcourt metropolis of Rivers State, Nigeria were examined for contamination with PAHs and BTEX. The concentration of the contaminants ranged from 0.601  $\pm$  0.001 – 3.678  $\pm$  0.036 mg/kg and < 0.001 – 0.013  $\pm$  0.003 for total PAHs and BTEX respectively. Soil sample D1 had the highest concentration of PAHs (3.678  $\pm$  0.036 mg/kg) and BTEX (0.013  $\pm$  0.003 mg/kg). The depth of the soil had no significant effect on the concentration of the contaminants. The concentration of BTEX was very small due to volatilization, dissolution, and degradation by microorganisms. All the samples were found to be contaminated with PAHs and BTEX. [Journal of American Science 2010;6(9):242-246]. (ISSN: 1545-1003).

Keywords: Soil, PAHs, BTEX, and Automobile mechanic activities.

## 1. Introduction

The major environmental concerns in urban and industrial areas are polycyclic aromatic hydrocarbons. Polycyclic aromatic hydrocarbons are a large group of organic compounds with two or more fused aromatic rings. They have a relatively low solubility in water, but are highly lipophilic. When dissolved in water or adsorbed on particulate matter, PAHs can undergo photodecomposition when exposed to ultraviolet light from solar radiation. In the atmosphere, PAHs can react with pollutants such as ozone, nitrogen oxides and sulphur dioxide, yielding diones, nitro- and dinitro-PAHs, and sulphonic acids, respectively. PAHs may also be degraded by some microorganisms in the soil (WHO, 1987; ASTDR, 1994).

PAHs pollutants have high molecular mass. PAHs of 4 and more condensed aromatic rings are considered to be more dangerous than two and three rings PAHs in view of their potentials (Tuhackova et al., 2001). PAHs are formed mainly as a result of pyrolytic process, especially the incomplete combustion of organic materials during industrial and other human activities, such as processing of coal and crude oil, combustion of natural gas, including for heating, combustion of refuse, vehicle traffic, cooking and tobacco smoking as well as in natural processes such as carbonization. Natural sources include release in forest or bush fires and from volcanic eruptions. Most environmental PAHs are products of incomplete combustion or pyrolysis of fossil fuels (Holbrook, 1990; Zou, 2003).

PAHs are present in smoke from wood fires, creositetreated wood products, cereals, grains, flour, bread, vegetables, fruits, meat, fish, processed or pickled foods, and contaminated cow's milk or human breast milk. Food grown in contaminated soil may also contain PAHs. Cooking meat or other food at high temperatures, which happens during grilling or charring, increases the amount of PAHs in the food. People living near waste site containing PAHs may be exposed through contact with contaminated air, water, and soil (ATSDR, 1995).

The movement of PAHs in the environment depends on properties such as how easily they dissolve in water, and how easily they evaporate into the air. PAHs in general do not easily dissolve in water. In soil, PAHs are most likely to stick lightly to particles. Some PAHs evaporate from surface soils to air. Certain PAHs in soils also contaminate underground water (ATSDR, 1995).

PAHs are known for their carcinogenic effects. The following PAHs are considered as human carcinogens: benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, indeno(1,2,3-cd)pyrene dibenz(a,h)anthracene, (Wcislo, 1998; ATSDR, 1990). Several of the PAHs, including benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno(1,2,3-c,d)pyrene, have caused tumors in laboratory animals when they breathed and ate these substances( ATSDR,1995). Mice fed with levels of benzo(a)pyrene during pregnancy had difficulty reproducing, birth defects and decreased body weight. Studies in animals have also shown that PAHs can cause harmful effects on skin, body fluids, and the body's system for fighting disease after both short and long – term exposure. These effects have not been reported in human beings (ATSDR, 1995).

Adverse hematological effects have been observed in animal following oral exposure to high doses of PAHs. Aplastic anaemia, pancytopenia, severe bone marrow depression with almost complete destruction of pluripotent haematopoietic stem cells have been seen in non-responsive mice after oral BaP, while extreme resistance to bone marrow toxicity was observed in responsive mice (Anselsletter and Heimpel, 1986)

In vitro experiments have demonstrated the cytoxicity of BaP and various other PAHs to cells from the lungs of experimental animals and humans. Severe, long –lasting hyperplasia and other adverse effects similar to the preneoplastic changes seen in vivo following exposure to PAHs have been observed (Richter *et al.*, 1985).

BTEX as an organic pollutant is an acronym for benzene, toluene, ethylbenzene, and xylene. This group of volatile organic compounds (VOCs) contaminate our soil through spills involving the release of petroleum products such as gasoline, diesel fuel, lubricating oil and heating oil from leaking oil tanks (Salanitro et al., 1997). They are common environmental contaminants. These compounds will tend to be dissolved in the water phase or evaporated into the air spaces of the soil because of the relatively high water solubility, low  $K_{ow}$ (octanol-water partition coefficient) values. They are not attenuated very much by the soil particles or constituents because of their high relative hydrophilic nature and can be transported several kilometers downstream the source.

BTEX appearance in soil and groundwater can be remediated by volatilization, dissolution, sorption (Bedient, 1994) and degradation by microorganisms (Schreiber and Bahr, 2002); natural attenuation (MacDonald, 2000) or in situ remediation (Cunnigham *et al.*, 2001).

In this present study, the level of soil contamination by PAHs and BTEX in automobile mechanics workshops in Port-Harcourt Metropolis of Rivers State, Nigeria were determined.

### 2. Materials and Methods

Soil samples were collected from various automobile mechanic workshops at different depths using soil augar in November 2009. The samples were labeled as follows: A1, A2, A3, A4, B1, B2, B3, B4, C1, C2, C3, C4, D1, D2, D3, D4, E1, E2, E3, E4. Where A, B, C, D and E represent Choba town, Mile 3, Rumuola, Trans-Amadi and Rumuokoro respectively. 1,2,3,and 4 represent the various depth 0 -5 cm, 5 - 10 cm, 10 - 2- cm, and 20 - 30 cm respectively. The control samples were collected from Forestry Research Institute Umudike, Nigeria at the same depths and were labeled F1, F2, F3, and F4.

### Sample Analysis

Soil PAH and BTEX extraction was carried out using the US EPA 3540 C and 3630 C method. The extraction of PAHs and BTEX from the soil was carried out in a soxhlet apparatus with 100 ml methylene – Chloride for 24 hours. The extract was reduced to 2 ml and dissolved in cyclohexane to 5 ml volume. The resulting extract was analyzed by HP 5870 gas chromatograph.

## 3. Results

Samples	1	2	3	4
А	0.873±0.003	$1.132 \pm 0.006$	1.022 ± 0.001	1.001 ± 0.002
В	$0.764 \pm 0.013$	$0.978 \pm 0.030$	0.601 ± 0.001	0.696 ± 0.037
С	$2.910 \pm 0.103$	1.671 ± 0.037	$2.041\pm0.170$	2.003 ± 0.096
D	$3.678 \pm 0.036$	$3.097 \pm 0.003$	2.987 ± 0.009	2.903 ± 0.103
Е	2.093 ± 0.138	$2.013 \pm 0.078$	$1.996\pm0.047$	1.879 ± 0.038
F	0.031 ± 0.001	0.017 ± 0.003	0.030 ± 0.001	0.027 ± 0.003

Table 1. Total PAHs concentrations of soil of some selected automobile Mechanic workshops in mg/kg

Results are mean  $\pm$  standard deviation of three determinations 1 = 0 - 5 cm, 2 = 5 - 10 cm, 3 = 10 - 20 cm, 4 = 20 - 30 cm

Samples	1	2	3	4
А	0.005 ± 0.001	0.005 ± 0.001	$0.004 \pm 0.001$	$0.003 \pm 0.001$
В	0.004 ± 0.001	0.006 ± 0.001	$0.006 \pm 0.002$	$0.007 \pm 0.002$
С	0.005 ± 0.001	0.006 ± 0.001	$0.007 \pm 0.002$	$0.008 \pm 0.002$
D	0.013 ± 0.003	$0.006\pm0.001$	0.006 ± 0.001	$0.005 \pm 0.001$
E	0.005 ± 0.001	0.003 ± 0.001	$0.001\pm0.001$	0.001 ± 0.001
F	< 0.001	< 0.001	< 0.001	< 0.001

Table 2. Total BTEX concentrations of soil of some selected automobile Mechanic workshops in mg/kg

Results are mean  $\pm$  standard deviation of three determinations 1 = 0 - 5 cm, 2 = 5 - 10 cm, 3 = 10 - 20 cm, 4 = 20 - 30 cm



Figure 1. Total PAHs concentrations of soil of some selected automobile mechanic workshops





### 4. Discussions

Concentration of the total PAHs found in the contaminated soils analyzed ranged from  $0.601 \pm 0.001 - 3.678 \pm 0.036$  mg/kg (table 1/ figure 1). The total PAHs concentration in soil from D1 ( $3.678 \pm 0.036$  mg/kg) was higher than the corresponding data from other sampling sites. This was attributed to the influence of the level of the automobile repair that is been carried out and town D is an industrial area in Port-Harcourt metropolis. The level of industries can also attribute to the high level of PAH concentration in the soils. The lowest concentration ( $0.601 \pm 0.001$ ) of the total PAHs was found in soil sample B3.

Soil samples collected from these areas were contaminated in varying degrees irrespective of the depths of the soil by automobile wastes dumps, oil or fuel spillage from heavy trucks and vehicles and burning gasoline and diesel by light and heavy vehicles. Because of the very low water solubility. PAHs will tend to be sorbed to the organic matter in the soil instead of being solubilized in the infiltrating water and through this, it will be transported downwards to the groundwater reservoirs. The sorption process is therefore counteractive to efficient biodegradation since it will decrease bio-availability due to sorption, the compounds will be located in micro porous areas of the soil making it inaccessible to the bacteria, and the biodegradation will thus be controlled by the slow desorptive and diffusive mass transfer into the biologically active areas (Zhang et al., 1998). PAH show very low aerobic degradability depending on the environmental conditions and available concentration. Only two - and three ringed compounds have been shown to be degraded under anaerobic conditions with nitrate or sulphate as the terminal electron acceptor (Coates et al., 1996).

The concentration  $(0.027 \pm 0.003 - 0.031 \pm 0.001 \text{ mg/kg})$  of these contaminants found in the control samples was less than the concentrations found in other samples. PAH concentrations in uncontaminated and contaminated soils have been reported (Dziewlecka et al., 1993; Kabata-Pendias et al., 1995; Maliszewsa-Kordybech and Smerczak, 1997; Terelak et al., 1995; Wcislo, 1998; Mira and Petar, 2004; Zou, et al., 2003; Olajire and Brack, 2005; Beg et al., 2003; Udoetok and Osuji, 2008).

From table 2, it was found that the concentrations of BTEX ranged from < 0.001 - 0.013 $\pm$  0.003 mg/kg. Sample D1 had the highest BTEX concentration while E3 and E4 had the lowest (<0.001 mg/kg). concentration The BTEX concentrations of the samples were very small. This is due to the characteristics of the contaminant such volatilization, dissolution, sorption as and degradation by microorganisms and also the time of the waste was dumped. The control sample had a BTEX concentration < 0.001 mg/kg. This is due to no industrial or agricultural practices and no automobile oil, diesel or fuel spill.

## Conclusion

The total PAHs and BTEX concentrations of soil samples of automobile mechanic workshops in Port-Harcourt metropolis ranged from  $0.601 \pm 0.001 - 3.678 \pm 0.036$  mg/kg and  $< 0.001 - 0.013 \pm 0.003$  respectively. Soil sample collected from an industrial area of the metropolis had a highest concentration of  $3.678 \pm 0.036$  mg/kg PAHs and  $0.013 \pm 0.003$  mg/kg BTEX compared to other samples. Depth of the soil was found not to have any significant effect on the concentrations of the contaminants. This is due to the characteristics of the contaminants such as volatilization, dissolution, degradation and adsorption of PAH to the organic matter of the soil. All the samples tested had PAHs content in varying concentrations and very trace amount of BTEX.

The study of soil PAHs and BTEX should extend to include soils in residential areas, schools, streets and markets, since these compounds are toxic and can be found in the environment.

### References

- Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological profile for polycyclic aromatic hydrocarbons (PAHs). 1990; T.P 90-20
- Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological profile for polycyclic aromatic hydrocarbons (PAHs). Atlanta, G.A: U.S. Department of Health and Human Services, Public Health Service 1994.
- Agency For Toxic Substances and disease Registry (ATSDR). Toxicological profile for polycyclic aromatic hydrocarbons (PAHs). Atlanta, G.A: U.S. Department of Health and Human Services, Public Health Service 1995.
- Anselstetter, V. and Heimpel, H. Acute hematotoxicity of Oral benzo(a)pyrene: The Role of the Ah locus. Acta haematologica Basel. 1986; 76: 217 – 223.
- Bedient, Philip B. Groundwater Contamination, Transport and Remediation, Prentice Hall PTR 1994.
- Beg, M.U., Saeed, T., Al Muzaini, S., Beg, K.R., and Al – Bahloul, M. Distribution of petroleum hydrocarbon in sediment from coatal area receiving industrial effluent in Kuwait. Ecotoxicology and Environmental safety. 2003; 54:47-55.

- Cunningham, J.A., Rahme, H., Hopkins, GD, Leborn, C., Reinhard, M. Enhanced in situ Bioremediation of BTEX Contaminated Ground Water by Combined Injection of Nitrate and Sulfate. Environ. Sci. Technol. 2001; 35, 1663 – 1670.
- Dziewiecka, B., Lukasik, K., Wcislo, E. (1993). A Method for Evaluation of Agricultural Areas Contaminated With Polycyclic Aromatic Hydrocarbons. Internal Report. Institute for Ecology of Industrial Areas, Katowice (in Polish).
- Holbrook, D.J. Carcinogenesis, in: Haddad, L. M and Chester, J.F. (Eds.): Clinical Management of poisoning and drug overdose, 2<sup>nd</sup> ed, W.B. Saunders Co. Philadelphia, PA, 1990; 508 – 521.
- Kabata-Pendias, A., Piotrowska, M., Motowicka-Terelak, T., Maliszewska-Kordybach, B., Filipiak, K., Krakowiak, A., Pietruch, CZ. Guidelines for Assessment of Soil Contamination-Heavy Metals, Sulphur and PAHs. Biblioteka monitoringunSrodowiska, Warszawa (in polish) 1995
- Maliszewsa-Kordybach, B., Smerczak, B. The Content of Polycyclic Aromatic Hydrocarbons (PAHs) in Agricultural Soils in Lublin District. Roczniki Gleboznawcze. T. 1997, (1 – 2), 95
- McDonald, J.A. Evaluating Natural Attenuation for Groundwater Cleanup. Environ. Sci. Technol. 2000; 34, 346A – 353A.
- Mira, M. Pucarevic, Petar D. Sekulic (2004). Polycyclic Aromatic Hydrocarbons and Pesticides in Soil of Vojvodin. Proc. Nat. Sci., Matica Srpska Novi Sad, 107: 93 – 100.
- Olajire, Abbas, A. and Brack, W. Polycyclic aromatic hydrocarbons in Niger Delta Soil: Contamination sources and Profiles. Int. j. Environ. Sci. tech. 2005; 2(4): 343 – 352.
- 15. Richter Reichhelm, H.B. et al. Scanning Electron Microscopic Investigations on the Respiratory Epithelium of the Syrian Golden Hamster. VI. In Vitro Effects of Different Polycyclic Aromatic Hydrocarbons. Zentralbalt fur Bakteriologische

02 / 17 / 2010

und Mikrobiologische Hygiene B. 1985; 181: 272 – 280.

- Salanitro, JP, Dorn, PB, Huesemaann, MH, Moore, KO, Rhodes, IA, Rice, JLM, Vipond, TE, Western, MM, Wisniewski, H.L. Crude oil Hydrocarbon and Soil Ecotoxicity Assessment. Environ. Sci. Technol. 1997; 31, 1769 – 1776.
- Schreiber, ME, Bahr, JM. Nitrate–Enhanced Bioremediation of BTEX – Contaminated Ground Water. Parameter Estimation from Natural-Gradient Tracer Experiments. J. contm. Hydrol. 2002; 55, 29 – 56.
- Terelak, H., Piotrowska, M., Motowicka-Terelak, T., Stuczynski, T., Maliszewska- Kordy Bach, B., Budzynska, K., Pietruch, CZ. Ecological status assessment of agricultural lands in the Czestochowa province. Internal Report. Istitute of soil science and plant cultivation, Pulawy (in polish) 1995
- Udoetok, I. A. and Osuji Leo C. Gas chromatographic fingerprinting of Crude oil from Idu – Ekpeye oil spillage site in Niger – Delta, Nigeria. Environ. Monit. Assess 2008; 141: 359 – 364.
- Wcislo, E. Soil Contamination with Polycyclic Aromatic Hydrocarbons (PAHs) In Poland – A Review. Polish journal of Environ. Studies 1998; 7(5): 267 – 272.
- 21. Wcislo, E., Kuperberg, M., Teaf, C. Risk assessment for the Czechowice oil Refinery Lagoons. Internal Report. Institute for Ecology of Industrial Area, Katowice 1997.
- World Health Organization Regional Office for Europe Polynuclear aromatic hydrocarbons (PAHs). In: Air quality guidelines For Europe. 1987; 105 – 117.
- Zou, Y.L., Zhan, W., Atkinskon, S. The characterization of polycyclic aromatic hydrocarbons emission from burning of different firewood species in Australia, Environmental pollution, 2003; 124: 283 – 589.