# Anions, Total Petroleum Hydrocarbons and Aromatic Hydrocarbons in Soils of Aba Dumpsites

## E. C. Ogoko[1*] and Kelle Henrietta Ijeoma[1]

[1]Chemistry Unit, School of Science and Technology, National Open University of Nigeria, PMB 80067, Victoria Island, Lagos, Nigeria.

*Authors' contributions*

*This work was carried out in collaboration between both authors. Author ECO, designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors ECO and KHI managed the analyses of the study and managed the literature searches. Both authors read and approved the final manuscript.*

*Original Research Article*

## ABSTRACT

This study was intended to evaluate the extent of contamination of soils in the vicinity of some selected dumpsites (Enyimba, Ogbor Hill and World Bank) in Aba Metropolis by anions (nitrate, sulphate and phosphate), polycyclic aromatic hydrocarbon and total petroleum hydrocarbon. Soil samples were obtained in triplicate on monthly intervals for three consecutive months during dry seasons in three different dumpsites and a neighborhood reference site (Aba North Industrial Layout). These soil samples were then analysed for anions, total aromatic hydrocarbons and total petroleum hydrocarbon. Analysis of total aromatic hydrocarbons and total petroleum hydrocarbons were performed by gas chromatographic method whereas spectrophotometer (model 2000) was used in evaluating nitrate, sulphate and phosphate concentrations in the soil samples. Nitrate content ranged from 980.0 to 2120.3 mg/Kg (Enyimba dumpsite), 850.25 to 1120.3 mg/Kg (Ogbor Hill Dumpsite) and 102.43 to 1980.72 mg/Kg (World Bank Dumpsite). Sulphate concentrations which ranged from 78.99 to 121.21 mg/Kg at the dumpsites were higher when compared to values

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*Corresponding author: E-mail: eogoko@noun.edu.ng;*

obtained from reference samples (21.65 to 94.50 mg/Kg). The levels of phosphate in the soil samples from the dumpsites ranged from 9.63 – 15.10 mg/Kg, 7.13 – 12.25 mg/Kg and 5.10 – 10.80 mg/Kg, in Enyimba Dumpsite, Ogbor Hill Dumpsite and World Bank Dumpsite respectively. The concentration of phosphate in the reference samples demonstrated lower values (2.78 – 5.80 mg/Kg) when compared with those from dumpsites. The total polycyclic aromatic hydrocarbons (PAHs) distribution in the dumpsites and the reference site were Enyimba dumpsite (3.27 to 4.32 mg/Kg), Ogbor Hill Dumpsite (2.51 to 3.85 mg/Kg), World Bank Dumpsite (2.15 to 3.98 mg/Kg) and Aba North Industrial Layout (0.05 to 0.09 mg/Kg) respectively. The concentration of TPH ranged from 102.7 to 1340.4 mg/Kg, 93.9 to 1107.3 mg/Kg and 99.10 to 1098 mg/Kg for Enyimba, Ogbor Hill and World Bank dumpsites respectively. The samples from Aba North Industrial Layout recorded the least concentration levels ranging from non detectable limits to 0.09 mg/Kg. The results however, revealed a depth-wise steady decrease in concentrations across the soil (depth) profile with Enyimba dumpsite having elevated levels of all the parameters evaluated when compared with other study stations. There was no contamination activity found in samples obtained from reference site (Aba North Industrial Layout) unlike in the dumpsites besides the levels of total petroleum hydrocarbon (TPH) indicates potent health risk in the environment of the dumpsites.

## 1. INTRODUCTION

There has been rapid increase in the quantity of municipal solid waste generated in most cities of the world especially in developing countries, due to increasing population and consumption of resources as a consequence of domestic, commercial, agricultural and industrial activities [1,2]. There are several methods of municipal waste treatment namely; landfills, incineration or combustion and open dump [3]. The practice of solid waste treatment is interconnected with quite a lot of unpleasant environmental consequences and enhances health risks to people living in such communities [4,5]. The most common method of municipal waste disposal in Nigeria is the open dumps which involves unsystematic disposal of solid waste in dumpsites situated within municipal areas [6]. These are open holes or field on the ground where trash, inert and recyclable wastes are disposed of with little or no adherence to the weak environmental regulation domicile in the area. The accumulated solid waste can be treated by burning at very high temperatures in order to have firm control of bacterial activities and effective weight volume reduction. It is pertinent to note that thermal combustion of solid waste is associated with air pollution in the vicinity of the open dumps. Several pollutants arising from fires as a result of various methods available for municipal waste treatments are very common hitherto have not received significant scholarly and media interest [7]. Biological decomposition of biodegradable components of the solid waste prior to burning, leads to emission of unacceptable odour and significant quantity of leachates. Besides, dumps sites are fertile breeding ground for snakes and disease vectors such as flies, mosquito and rodents [8]. Increase in population of these vectors in the open dump will inadvertently increase the health risk of the people living in the immediate environment of the dump site. Diseases such as cholera, diarrhea, dysentery, typhoid fever, malaria and Lassa fever could be prevalence in such areas since they are transmitted by these vectors.

As rain water moves through the refuse in an open dump, it readily absorbs many organic and inorganic compounds present in the refuse. The inorganic pollutants of soil within an open dump are sulphates, nitrates, phosphates and essentially heavy metals such as lead, arsenic, mercury, chromium, nickel, copper, and zinc amongst others. Petroleum hydrocarbons, bisphenol A, polycyclic aromatic hydrocarbons and phthalates has earlier been reported in landfill leachate [9-12]. Some of these organic compounds can be evaluated as total polycyclic hydrocarbons (PAHs) and total petroleum hydrocarbons (TPH) in this work. Polycyclic aromatic hydrocarbons are an omnipresent family of several related environmental persistent organic compounds of various structures and with different levels of toxicity. Total petroleum hydrocarbon is an index used to measure the gross quantity of petroleum hydrocarbon products present in the environment rather than seeking to measure individual component separately [13,14]. These toxic leachates drain into the soil below the dump and could eventually

enter and contaminate the ground water. The run-off water from these open dumps pollutes close by water as well as land [15]. The presence of huge amount of methane in the environment is detrimental to health and constitutes hazards because of its excellent ability to explode in the presence of flame. Open dumps serve as a source of organic manure to small scale farmers who grew crops on nearby lands and ultimately turn them to the market for consumption. The commonest route by which pollutants invade the human body is by means of contaminated agricultural plants and food products, animals as well as water [5].

The aim of this study is therefore to evaluate the levels and associated health risk of total petroleum hydrocarbon, polycyclic hydrocarbons and anions in the soils within the vicinity of dumpsites.

## 2. MATERIALS AND METHODS

### 2.1 Study Area and Data Collection

This study was carry out in Aba, the commercial nerve centre of Abia State situated in south eastern Nigeria. Aba consists of several large markets, vast farming lands as well as a good number of small to medium scale industries and the residents are known for their artisan and industrious nature. Aba metropolis is however located within the coordinates 5° 07`N and 7° 22' E, and surrounded by four other states (Imo, Enugu, Akwa Ibom and Rivers), as the location map is shown in Fig. 1.

Three different dumpsites were identified for this study. They are Enyimba, Ogbor Hill and World Bank Area. Similarly a neighborhood soil,
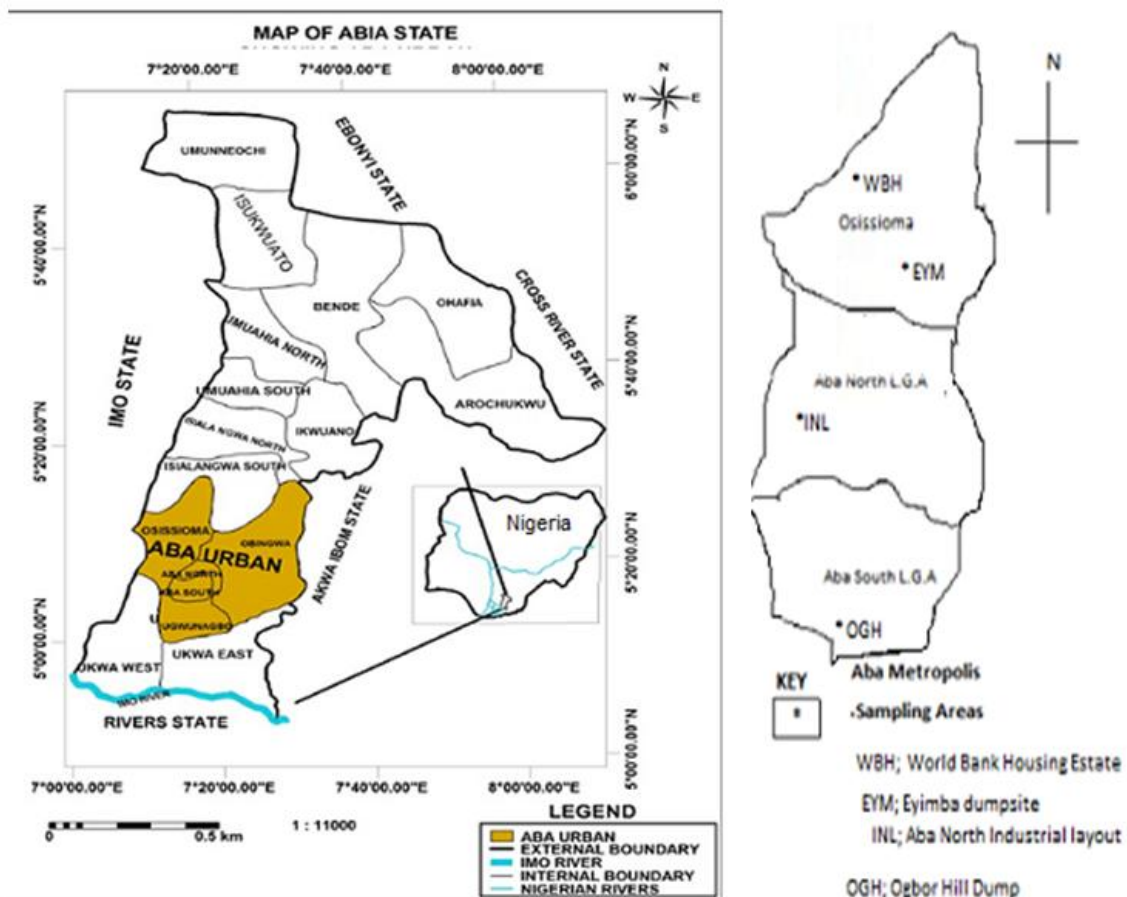


**Fig. 1. Abia state Map (Nigerian) showing Aba Metropolis and sampling areas (Adapted from Nwoko Alex, 2013 and Ogoko et al. 2015)**

Aba North Industrial Layout (Control) was selected as the reference soil, and evaluated for the purpose of comparison. Each study site was initially divided into four quadrants and three samples were collected from each quadrant at depth of 0 -15 cm, 15 - 30 cm and 30 – 45 cm and then pooled to form composite samples respectively. The sampling procedure was repeated each month for three consecutive months during the dry season (December, 2014 to February, 2015) for all the dumpsites as well as the control site. The samples were autoclaved for 10 min (110°C), according to method of Razavi and Lakzian [16], and then stored in sterile polyethene bags prior to Analysis.

## 2.2 Sample Analysis

### 2.2.1 Extraction procedure of Total Petroleum Hydrocarbon (TPH)

Anhydrous sodium sulphate was added into an extracting bottle containing 10 g of previously homogenized and sterilized soil samples and the mixture was stirred vigorously. 300 µg/mL of 1-chlorooctadecane (surrogate standard) was added to the sample. 30 mL of dichloromethane was added in the extracting bottle containing the sample and the bottle tightly corked before transferring it to a mechanical shaker. The sample was allowed to settle for 1 h after agitation for 5 hour at room temperature in the mechanical shaker. The sample was filtered and the filtrate was allowed to concentrate to 1 mL by evaporation overnight in a fume chamber. [17,18].

### 2.2.2 Analysis of Total Petroleum Hydrocarbon (TPH)

The separation and detection of compounds in the soil was carried out using Agilent 6890N Gas Chromatography- Flame Ionization Detector instrument. 3 µL of concentrated sample that was previously eluted from column was injected into Gas chromatograph. The micro-syringe of GC was first rinsed with dichloromethane (blank) and further rinsed with the sample prior to sample analysis. Separation of sample into constituent compounds was achieved by injection of sample into the chromatographic column. The compounds after separation were passed through a flame ionization detector for detection and the amount of Analysis of Total Petroleum Hydrocarbon (TPH) was resolved at a particular chromatogram in mg/Kg [17,19].

### 2.2.3 Extraction procedure of total Polycyclic Aromatic Hydrocarbons (PAHs)

The total Polycyclic Aromatic Hydrocarbons (PAHs) was extracted and analyzed according to the method described by Nor et al. [20]. 500 mg of soil sample was dissolved in 25 mL n-hexane and acetone 7:3 (v/v). The extractions were done with the pressurized microwave extraction system under control pressure, and over a period of about 40 minutes. The equipment was allowed to cool down at room temperature after extraction which was followed by filteration using whatman glass fibre filters and kept in 25 mL universal bottles. The samples were concentrated by use of rotary evaporator to 1 mL.

### 2.2.4 Analysis of total Polycyclic Aromatic Hydrocarbons (PAHs)

Measurement of PAHs concentrations was done by the use of chromatography mass spectrometer equipped (Perkin Elmer Clarus) with elite column. The carrier gas was helium and a constant flow rate of 1 mL/min was maintained and the amount of Polycyclic Aromatic Hydrocarbons (PAHs) was resolved at a particular chromatogram in mg/Kg.

### 2.2.5 Determination of nitrate

The determination of nitrate in each of the previously extracted soil sample solutions was performed using spectrophotometer (model 2000) at a wavelength of 543 nm [21]. The instrument automatically selected the stored programme for nitrate (64 Nitrate-N) and values obtained were converted to ppm Nitrate ($NO_3^-$) by multiplying by 4.4 (conversion factor). The concentrations of nitrate in the samples were calculated from equation 2 and values shown in Tables 1-4.

$$NO_3^- (\mu g g^{-1}) = C \times V/M \qquad (2)$$

Where C is the concentration of $NO_3^-$ in the sample (ppm), V is the total volume of sample solution (100 mL) and M is the weight of the sample (1 g).

### 2.2.6 Determination of sulphate and phosphate

Sulphate content of the samples were determined by standard methods [21,22], whereas the concentration of phosphate was

determined via the method described by Dewis and Freitas [23].

## 3. RESULTS AND DISCUSSION

Result of $NO_3^-$, $SO_4^{2-}$, $PO_4^{3-}$, PAHs and TPH obtained from soil analysis were presented in Tables 1-4 accordingly. Nitrate ($NO_3^-$) concentration ranged from 980.00 to 2120.30 mg/Kg (Enyimba), 850.25 to 1120.30 mg/Kg (Ogbor Hill), and 102.43 to 243.40 mg/Kg (World Bank Area). These values were higher than the nitrate levels (81.39 to 1980.72 mg/Kg) obtained in the reference soil (Aba North Industrial Layout). The levels of nitrate tend to decrease across the soil profile with maximum values recorded at soil profiles 0 – 15 cm and minimum values obtained at soil depth of 30 – 45 cm. In a similar study conducted on Njoku Sawmill Waste Dumpsite in Owerri Municipal, the concentrations of nitrate ranged from 12.98 – 18.82 mg/Kg [24], however, this range of values were extreme lower than those obtained in this work.

The nitrate content of the test soils increased with increase dumping or pollution. Organic matter content in the dumpsite is broken down exothermically by the presence of microorganism, through a two steps process, initially into ammonia (ammonification) and subsequently to nitrate (nitrification). Nitrate has excellent mobility and leaches in the presence of water in to the soil and may percolate to an underlying aquifer [25]. High levels of nitrates in animals could readily converts into nitrites which form methemoglobin by binding favourably with heamoglobin and consequently interfering with the blood oxygen transfer [26]. Rapid and breathing difficulties, tremors and death are the most obvious symptoms of acute nitrate toxicity.

Similarly, the Sulphate ($SO_4^{2-}$) content of the soil samples exhibited the highest value in Enyimba Dumpsite (121.2 mg/Kg) and least in Ogbor Hill Dumpsite (78.99 mg/Kg). These values were higher than those obtained from samples from the control site (Aba North Industrial Layout), but interestingly a similar trend of depth-wise steady decrease in sulphate concentration across soil profile was observed in all the dumpsite as well as in the reference station.

**Table 1. Polycyclic aromatic hydrocarbon, TPH and anions in Enyimba dumpsite (mg/Kg)**

| Dept (CM) | | $NO_3^-$ | $SO_4^{2-}$ | $PO_4^{3-}$ | TPAH$_S$ | TPH |
|---|---|---|---|---|---|---|
| 0 – 15 | Mean | 2120.30 | 121.20 | 15.10 | 4.32 | 1340.40 |
| | Max | 2121.30 | 122.00 | 15.20 | 4.34 | 1341.70 |
| | Min | 2119.30 | 120.40 | 15.00 | 4.30 | 1339.10 |
| | SD | 0.82 | 0.65 | 0.10 | 0.02 | 1.06 |
| 15 – 30 | Mean | 1760.00 | 107.97 | 13.50 | 2.60 | 650.40 |
| | Max | 1762.00 | 108.97 | 13.70 | 2.71 | 651.10 |
| | Min | 1758.00 | 106.97 | 13.30 | 2.49 | 649.70 |
| | SD | 0.82 | 0.84 | 0.20 | 0.00 | 0.57 |
| 30 – 35 | Mean | 980.00 | 88.94 | 9.63 | 3.27 | 102.70 |
| | Max | 981.00 | 89.94 | 9.72 | 3.28 | 103.40 |
| | Min | 979.00 | 87.94 | 9.54 | 3.26 | 102.00 |
| | SD | 0.82 | 0.82 | 0.09 | 0.01 | 0.57 |

**Table 2. Polycyclic aromatic hydrocarbon, TPH and anions in Ogbor Hill dumpsite (mg/Kg)**

| Depth (CM) | | $NO_3^-$ | $SO_4^{2-}$ | $PO_4^{3-}$ | TPAH$_S$ | TPH |
|---|---|---|---|---|---|---|
| 0 – 15 | Mean | 1120.30 | 101.00 | 12.25 | 3.85 | 1107.30 |
| | Max | 1122.10 | 102.00 | 12.50 | 3.89 | 1110.00 |
| | Min | 1118.50 | 100.00 | 12.00 | 3.81 | 1104.60 |
| | SD | 0.90 | 0.82 | 0.25 | 0.03 | 2.70 |
| 15 – 30 | Mean | 1350.5 | 81.35 | 10.20 | 3.29 | 630.50 |
| | Max | 1351.5 | 82.00 | 10.35 | 3.49 | 631.50 |
| | Min | 1349.5 | 80.70 | 10.05 | 3.09 | 629.50 |
| | SD | 0.82 | 0.53 | 0.15 | 0.16 | 0.82 |
| 30 – 45 | Mean | 850.25 | 78.99 | 7.13 | 2.51 | 93.90 |
| | Max | 851.00 | 79.99 | 7.20 | 2.52 | 94.00 |
| | Min | 849.50 | 77.99 | 7.06 | 2.54 | 93.80 |
| | SD | 0.61 | 0.82 | 0.07 | 0.01 | 0.08 |

**Table 3. Polycyclic aromatic hydrocarbon, TPH and anions in world bank dumpsite (mg/Kg)**

| Depth (CM) | | $NO_3^-$ | $SO_4^{2-}$ | $PO_4^{3-}$ | $TPAH_S$ | TPH |
|---|---|---|---|---|---|---|
| 0 – 15 | Mean | 1980.75 | 109.43 | 10.80 | 3.98 | 1098.00 |
| | Max | 1981.95 | 109.63 | 11.60 | 4.01 | 1099.00 |
| | Min | 1979.55 | 109.23 | 10.00 | 3.95 | 1097.00 |
| | SD | 0.98 | 0.16 | 0.80 | 0.03 | 0.83 |
| 15 – 30 | Mean | 1492.51 | 97.69 | 6.20 | 3.10 | 671.60 |
| | Max | 1493.71 | 97.71 | 6.30 | 3.32 | 672.00 |
| | Min | 1491.31 | 97.69 | 6.10 | 2.90 | 671.20 |
| | SD | 0.98 | 0.01 | 0.10 | 0.16 | 0.33 |
| 30 – 45 | Mean | 102.43 | 79.59 | 5.10 | 2.15 | 99.11 |
| | Max | 103.23 | 80.79 | 5.24 | 2.17 | 99.20 |
| | Min | 101.63 | 78.39 | 4.96 | 2.13 | 98.91 |
| | Sd | 0.65 | 0.98 | 0.14 | 0.02 | 0.13 |

**Table 4. Polycyclic aromatic hydrocarbon, TPH and anions in Aba north industrial layout (mg/Kg)**

| Depth (CM) | | $NO_3^-$ | $SO_4^{2-}$ | $PO_4^{3-}$ | $TPAH_S$ | TPH |
|---|---|---|---|---|---|---|
| 0 – 15 | Mean | 243.40 | 94.50 | 5.80 | 0.05 | 0.09 |
| | Max | 244.30 | 95.50 | 6.00 | 0.06 | 0.11 |
| | Min | 242.50 | 93.50 | 5.60 | 0.04 | 0.07 |
| | SD | 0.74 | 0.82 | 0.20 | 0.01 | 0.02 |
| 15 – 30 | Mean | 230.50 | 77.60 | 3.84 | 0.003 | ND |
| | Max | 231.10 | 78.61 | 3.90 | 0.004 | ND |
| | Min | 229.90 | 76.61 | 3.78 | 0.002 | ND |
| | SD | 0.49 | 0.82 | 0.06 | 0.001 | ND |
| 30 – 45 | Mean | 81.39 | 21.65 | 2.78 | 0.09 | ND |
| | Max | 82.40 | 22.85 | 2.90 | 0.10 | ND |
| | Min | 80.38 | 20.45 | 2.66 | 0.08 | ND |
| | SD | 0.83 | 0.98 | 0.12 | 0.010 | ND |

The levels of phosphate in the soil samples from the dumpsites ranged from 5.10 – 10.80 mg/Kg, 7.13 – 12.25 mg/Kg and 9.63 – 15.10 mg/Kg in World Bank Dumpsite, Ogbor Hill Dumpsite and Enyimba Dumpsite respectively. The concentration of phosphate in the reference site used as control (Aba North Industrial Layout), ranged from 2.78 – 5.80 mg/Kg indicating lower values compared with those obtained from samples from dumpsite. High levels of Phosphate in the mammalian body could enhance aging process by causing tissue damages [27]. Toxicity of phosphate is also linked to impaired renal function, rhabdomyolysis and tumour lyndrome [28].

From Tables 1 to 4, the total polycyclic aromatic hydrocarbons (PAHs) distribution in the dumpsites and the reference site ranged between 3.270 to 4.320 mg/Kg (Enyimba Dumpsite), 2.510 to 3.852 mg/Kg (Ogbor Hill Dumpsite) and 2.150 to 3.98 mg/Kg (World Bank Dumpsite). The PAHs content of soils from Aba North Industrial Layout (control) was far below those of the three dumpsites investigated indicating pollution of soils of the dumpsites. The high PAHs concentration recorded at the dumpsites compared with the reference (Aba North Industrial Layout) soil may be a consequence of combustion of solid wastes emanated from commercial, industrial, agricultural activities as well as domestic refuse. PAHs are group of dangerous organic compounds which are known for their mutagenic, carcinogenic and teratogenic properties. PAHs concentrations in the samples were however, below the maximum recommended limit of 5 mg/Kg [29]. The total petroleum hydrocarbon (TPH) content of soils from all the dumpsites studied fascinatingly revealed high levels of concentration compared to the reference (Aba North Industrial Layout) site. The highest concentration values of TPH were found at Enyimba Dumpsite (102.70 to 1340.40 mg/Kg) followed by Ogbor Hill Dumpsite (93.90 to 1107.3 mg/Kg) while the lowest values were obtained at World Bank Dumpsite (99.10 to 1098.00 mg/Kg). The Aba North Industrial Layout (control) site

recorded the least concentration ranging from non detectable limits to 0.090 mg/Kg). The top soil profile (0-15 cm) recorded higher TPH values than the recommended maximum limit of 1000 mg/Kg by directorate of petroleum resources [30], and Australian standard [31]. It is quite instructive to note that the TPH content for most of the soil samples (dumpsites) studied indicates appreciable higher values compared to the corresponding PAHs content. This trend was not unexpected because TPH value is the sum total of PAHs and other organic compounds (fractions) that are of petroleum origin present at sites examined. The dumpsites could have been contaminated with automobile waste from mechanic workshops in addition to other waste sourced from increasing commercial, industrial and agricultural operations going on in the area.

## 4. CONCLUSION

From the study conducted and the data obtained, the presence of nitrate, sulphate, phosphate and polycyclic aromatic hydrocarbons were detected in the soils of the dumpsites. It was also established that the concentration levels of Nitrate ($NO_3^-$), Sulphate ($SO_4^{2-}$), $PO_4^{3-}$, PAHs and TPHs were generally higher in soils of the dumpsites than those of the reference site (Aba North Industrial Layout), indicating contamination of soils of the dumpsites.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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