

ANIONS AND TOTAL PETROLEUM HYDROCARBONS IN SOILS OF ABA DUMPSITES.

ABSTRACT

This study attempt to evaluate the extent of contamination of soils in the vicinity of some selected dumpsites in Aba Metropolis (Abia State), Nigeria by anions (NO_3^- and SO_4^{2-}), polycyclic aromatic hydrocarbon and total petroleum hydrocarbon. Analysis of total aromatic hydrocarbons and total petroleum hydrocarbons were determined by gas chromatographic method whereas spectrophotometer (model 2000) was used in evaluating NO_3^- and SO_4^{2-} concentration in the soil samples. Nitrate content ranged from 980.0 to 2120.3 mg/kg (EYM), 85025.0 to 1120.3 mg/kg (OSM) and 81.39 to 1980.72 mg/kg (WDH). Sulphate concentrations which ranged from 121.21 to 78.99 mg/kg at the dumpsites were higher when compared to values for reference samples (21.65 to 94.50 mg/kg). The total polycyclic aromatic hydrocarbons (PAHs) distribution in the dumpsites and the reference site were EYM (3.270 to 4.320 mg/kg), OSM (2.510 to 3.852 mg/kg), WDB (2.150 to 3.980 mg/kg) and NINL (0.003 to 0.090 mg/kg) respectively. The concentration values of TPH ranged from 102.7 to 1340.4 mg/kg, 93.90 to 1107.3 mg/kg and 99.10 to 1098 mg/kg for EYM, OSM and WDB dumpsites respectively. The NINL site recorded the least concentration levels ranging from non detectable limits to 0.090 mg/kg. There was no contamination activity found in samples obtained from reference site (NINL) but the concentration levels TPH indicates potent health risk in the environment of the dumpsites.

Key Words: Dumpsite, polycyclic aromatic hydrocarbon, contamination.

INTRODUCTION

Growing quantity of municipal solid waste are generated in most cities of developing countries, with Nigeria inclusive, due to increasing consumption of resources as a consequence of domestic, commercial and industrial activities. The most common method of municipal waste disposal in Nigeria is the open dumps. 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 could 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. 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 (Gochfeld M., 1995). 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. Some of these organic compounds can be evaluated as total polycyclic hydrocarbons (PAHs) and total petroleum hydrocarbons (TPH). 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. These toxic leachates drain into the soil below the dump and could eventually enter and contaminate the ground water. 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. The levels and associated health risk of total petroleum hydrocarbon, polycyclic hydrocarbons and anions in the dumpsites which serves as a source of manure to small scale farmers who grew crops and ultimately turn them into the market for consumption is of serious concern in this study.

MATERIALS AND METHODS

SAMPLE COLLECTION AND PREPARATION

The study was performed in Aba, Abia State of Nigeria. Aba is the commercial nerve centre of southern east Nigeria with several large markets and industries, ranging from small to medium scale industries. Residents of this town are known of their artisan and industrious nature. Three different dumpsites were identify and preferred for this study. They are Enyimba (EYM), Osisoma (OSM) and World Bank (WDB) dumpsites. A reference site (NINL) which is located at the outskirt of Aba Metropolis (National Institute of Nigerian Languages, OgborHill) was also selected for the study.

Soil samples were obtained from the dumpsites and the reference site with the aid of depth calibrated soil auger. Samples were then collected in sterile polyethene bags at soil depths of 0-15cm, 15-30cm and 30-45cm respectively during the dry season (December, 2014 to February, 2015).

EXTRACTION PROCEDURE TPH

Anhydrous sodium sulphate was added into an extracting bottle containing 10g of previously homogenized 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. (LAWI, 2011; Alinnor and Nwachukwu, 2013).

ANALYSIS OF TPH

The separation and detection of compounds in the soil was carried out using Agilent 6890N Gas Chromatography- Flame Ionization Detector instrument. 3µl 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 TPH was resolved at a particular chromatogram in mg/kg (LAWI, 2011; Cortes et al., 2012; Alinnor and Nwachukwu, 2013).

EXTRACTION PROCEDURE PAHS

The PAHs (total) was extracted and analyzed according to the method described by Nor et al, (2013). 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 filtration using whatman glass fibre filters and kept in 25 ml universal bottles. The samples were concentrated by use of rotary evaporator to 1 ml.

ANALYSIS OF 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 1ml/min was maintained and the amount of PAHs was resolved at a particular chromatogram in mg/kg.

DETERMINATION OF NITRATE AND SULPHATE

The determination of nitrate in each of the previously extracted soil sample solutions was performed using spectrophotometer (model 2000) at a wavelength of 543nm.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 concentration of nitrate in the samples were calculated from equation 2 and values shown in Table 1-4.

$$\text{NO}_3^- (\mu\text{gg}^{-1}) = C \times V/M \quad (2)$$

Where C is the concentration of NO_3^- in the sample (ppm), V is the total volume of sample solution (100ml) and M is the weight of the sample (1g). Sulphate contents of the samples were determined by standard methods [US EPA, 1980].

RESULTS AND DISCUSSION

Result of NO_3^- , SO_4^{2-} PAHs and TPH are presented in Table 1- 4 accordingly. The result however, revealed a depth-wise steady decrease in concentration with highest values noticeable at soil samples obtained from EYM dumpsite and least values of concentration at NINL site.

Nitrate (NO_3^-) concentration ranged from 980.00 to 2120.30 mg/kg (EYM), 850.25 to 1120.30mg/kg(OSM), 81.39 to 1980.72mg/kg (WDH) and 102.43 to 243.40mg/kg (NINL) .

Table 1: Polycyclic Aromatic Hydrocarbon, TPH and Anions in Enyimba Dumpsite (EYM)

Dept (cm)		NO ₃ ⁻	SO ₄ ²⁻	TPAHs	TPH
0-15	Mean	2120.30	121.20	4.32	1340.40
	Max	2121.30	122.00	4.34	1341.70
	Min	2119.30	120.40	4.30	1339.10
	SD	0.817	0.645	0.016	1.062
15 - 30	Mean	1760.00	107.97	2.60	650.40
	Max	1762.00	108.97	2.71	651.10
	Min	1758.00	106.97	2.49	649.70
	SD	0.816	0.837	0.001	0.572
30 -45	Mean	980.00	88.94	3.27	102.70
	Max	981.00	89.94	3.28	103.40
	Min	979.00	87.94	3.26	102.00
	SD	0.817	0.817	0.010	0.5650

Table 2: Polycyclic Aromatic Hydrocarbon,TPH and Anions in Osisioma Dumpsite(OSM)

Depth(cm)		NO ₃ ⁻	SO ₄ ²⁻	TPAHs	TPH
0-15	Mean	1120.30	101.00	3.85	997.30
	Max	1122.10	102.00	3.89	998.30
	Min	1118.50	100.00	3.81	996.30
	SD	0.900	0.817	0.033	0.817
15 - 30	Mean	1350.5	81.35	3.285	630.50
	Max	1351.5	82.00	3.49	631.50
	Min	1349.5	80.70	3.09	629.50
	SD	0.817	0.531	0.163	0.817
30 -45	Mean	850.25	78.99	2.51	93.90
	Max	851.00	79.99	2.52	94.00
	Min	849.50	77.99	2.54	93.80
	SD	0.612	0.817	0.01	0.082

Table 3: Polycyclic Aromatic Hydrocarbon, TPH and Anions in World Bank Dumpsite (WDB)

Dept (cm)		NO ₃ ⁻	SO ₄ ²⁻	TPAHs	TPH
0-15	Mean	1980.75	109.43	3.98	1098.00
	Max	1981.95	109.63	4.01	1099.00
	Min	1979.55	109.23	3.95	1097.00
	SD	0.98	0.163	0.025	0.817
15 - 30	Mean	1492.51	97.69	3.10	671.60
	Max	1493.71	97.71	3.32	672.00
	Min	1491.31	97.69	2.90	671.20
	SD	0.979	0.005	0.163	0.327
30 -45	Mean	81.39	79.59	2.15	99.11
	Max	82.40	80.79	2.17	99.20
	Min	80.38	78.39	2.13	98.91
	SD	0.825	0.979	0.016	0.125

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127 **Table 4:** Polycyclic Aromatic Hydrocarbon, TPH and Anions in Ogbor Hill (NINL)

Dept (cm)		NO ₃ ⁻	SO ₄ ²⁻	TPAHs	TPH
0-15	Mean	243.40	94.50	0.05	0.09
	Max	244.30	95.50	0.06	0.11
	Min	242.50	93.50	0.04	0.07
	SD	0.735	0.815	0.012	0.016
15 - 30	Mean	230.50	77.60	0.003	ND
	Max	231.10	78.61	0.004	ND
	Min	229.90	76.61	0.002	ND
	SD	0.489	0.817	0.001	ND
30 -45	Mean	102.43	21.65	0.09	ND
	Max	103.23	22.85	0.10	ND
	Min	101.63	20.45	0.08	ND
	SD	0.653	0.979	0.010	ND

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129 The nitrate content of the test soils increased with increase dumping or pollution. Organic matter
 130 content in the dumpsite is broken down exothermically by the presence of microorganism,
 131 through a two steps process, initially into ammonia (ammonification) and subsequently to nitrate
 132 (nitrification). Nitrate has excellent mobility and leaches in the presence of water in to the soil

and may percolate to an underlying aquifer (Osu and Ogoko, 2012). Similarly, the Sulphate (SO_4^{2-}) content of the soil samples tested tends to record the highest value in EYM (121.210 mg/kg) and least in NINL (94.500 mg/kg).

From Table 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 (EYM), 2.510 to 3.852 mg/kg (OSM) and 2.150 to 3.980 mg/kg (WDB). The PAHs content of soils from NINL was far below those of the three dumpsites investigated. The high PAHs concentration recorded at the dumpsites 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 (ANEC, 1992). The total petroleum hydrocarbon (TPH) content of soils from all the dumpsites studied fascinatingly revealed high levels of concentration compared to the reference (NINL) site. The highest concentration values of TPH were found at EYM (102.70 to 1340.40 mg/kg) followed by OSM (93.90 to 1107.3 mg/kg) while the lowest values were obtained at WDB (99.10 to 1098.00 mg/kg). The NINL site recorded the least concentration ranging from non detectable limits to 0.090 mg/kg). The top soil profile (0-15cm) recorded TPH values higher than the recommended maximum limit of 1000 mg/Kg by directorate of petroleum resources (DPR 2000) and Australian standard (NSW, 2009). 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.

CONCLUSION

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

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