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ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS IN STREET SOIL DUST IN KUMASI METROPOLIS OF GHANA

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Abstract. Concentrations of polycyclic aromatic hydrocarbons (PAHs) in street soil dust from streets in Kumasi Metropolis in the Ashanti Region of the Republic of Ghana have been measured in this study. The concentrations of the various types of PAHs identified in this study are as follows: Naphthalene (m/e 128) – 41,700 μg/kg, Acenaphthylene (m/e 152) – 99,300 μg/kg, Acenaphthene (m/e 154) – 111,200 μg/kg, Fluorene (m/e 166) – 8,900 μg/kg, Carbazole (m/e 167) – 3,500 μg/kg, phenanthrene (m/e 178) – 12,900 μg/kg, Anthracene (m/e 178) – 5,400 μg/kg, Fluoranthene (m/e 202) – 16,200 μg/kg, Pyrene (m/e 202) – 15,000 μg/kg, Benzo[a]anthracene (m/e 228) – 13,800 μg/kg, Chrysene (m/e 228) – 33,600 μg/kg, Benzo[k]fluoranthene (m/e 252) – 45,700 μg/kg, Benzo[a]pyrene (m/e 252) – 27,900 μg/kg, Perylene (m/e 252) – 57,200 μg/kg and Benzo[g, h, i]perylene (m/e 276) – 47,000 μg/kg. The results of the study shows that road users, like resident living in buildings within these areas, those engaged in commercial activities like hawking, and the general public are at risk of exposure to the toxic effects of the various types of PAHs from the exhaust of vehicles into the environment. According to these results, there is the potential for exposure to high levels of PAHs for road users and those living in urban environments or along highways.

Keywords: Kumasi, p–terphenyl–d10 (m/e 244), PAH.

1. Introduction

High urbanization and industrialization growth have made Kumasi one of the most densely populated cities in Ghana. This has resulted in an increase in the number of vehicles that ply the metropolis each day. Uncontrolled emissions from industries and exhaust of vehicles have increased the levels of pollutant in the metropolis. Emissions from vehicles contain a variety of toxic chemicals such as platinum and palladium from catalytic converters, lead from vehicles that run on leaded fuels, nickel from vehicles that also run on diesel, cadmium and zinc from vehicular tyres and copper from brakes linings and electrical wires. In addition to the above toxic chemicals from vehicular fallouts is that of polycyclic aromatic hydrocarbons (PAHs).

Polycyclic aromatic hydrocarbons (PAHs) occur ubiquitously in the environment and can be found in sediments, soils and water either in solution or adsorbed on particulate material (Alloway and Ayres, 1993). Most PAHs in the environment are from incomplete burning of carbon – containing materials like oil, wood, garbage or coal. Many useful products such as mothballs, blacktop, and creosote wood preservatives contain PAHs. They are also found at low concentrations in some special – purpose skin creams and anti–dandruff shampoos that contain coal tars (Wisconsin Department of Health, 2000).

Automobiles exhaust, industrial emission and smoke from burning of wood, charcoal and tobacco contain high levels of PAHs. It is in the light of this that this study was conducted to determine the levels and the various types of PAHs in vehicular fallouts in the Kumasi metropolis.

Automobile exhaust from the combustion of fossil fuels releases large concentrations of different types of PAHs into the ambient air in Kumasi along highways or high, low or medium vehicular densities.

The PAHs released from the fallouts of vehicular movement in Kumasi may be inhaled by road users such as hawkers, or are deposited on nearby vegetations or soils, buildings, food stuffs sold along these traffic points. Some of the PAHs may also settle on the skin of resident road users in Kumasi, which may cause redness, blistering and peeling (Wisconsin Department of Health, 2000).

Studies conducted in developed countries such as USA, Japan, etc, have revealed that the concentration of Bezo[a]pyrene in vehicular fallout is between 0.0063ppb to 1.9×10^{-6} ppb. Kuniko (1988), measured the BaP and PAH in airborne particulates near a high way in Tokyo, Japan during December, 1984 within 60 m radius from a crossing point of two high ways. The BaP concentration in precipitated dust was 1.49×10^{-4} to 1.3×10^{-4} ppb. However, no studies have been conducted in Ghana to measure the concentrations of PAHs in ambient air in municipal and metropolitant cities. It is in light of this that this study was conducted. The following health effects may occur after several years of exposure to PAHs such as benzo[a]pyrene:

- Reproductive effects: reproductive problems and problems in unborn babies' development have occurred in laboratory animals that have been exposed to benzo[a]pyrene. The health effects of other PAHs on reproductive organs of human beings and laboratory animals are not well known.
- Other organs and systems of human beings can be damaged after long exposure to benzo[a]pyrene and other PAHs whose mode of action is not well known (Wisconsin Department of Health, 2000).

This study was designed to measure the concentrations of the various types of PAHs that are deposited in soil dusts taken from different traffic point in Kumasi metropolis.

The main thrust for this study is to:

- Identified the various types of PAHs from vehicular movement in Kumasi metropolis.
- Determine the concentrations of each type of PAH identified from the fallout due to vehicular movement in Kumasi metropolis.

- Compare the concentrations of the various types of PAHs obtained in this study with permissible standards recorded in other countries.

2. Materials and Methods

2.1. Sampling techniques

Random sampling technique was adopted in obtaining soil samples from road dusts from each of the major traffic points in the metropolis. In all 128 soil samples were taken from different streets in Kumasi Metropolis.

The soil samples were put together after which a representative sample (laboratory sample) was obtained from the composite sample.

2.2. Sample collection and preparation

The samples were obtained from street dust from each of the four zones. The samples were put into amber glass containers and sealed with an aluminium foil. The samples were stored in an ice – chest at 4°C and conveyed to the laboratory. In the laboratory the samples were freed from stones and other foreign materials. The samples were then air – dried to a constant weight, ground with motor and pestle and then sieved through a 200 μm mesh.

2.3. Analysis of PAHs

10 g of a crushed, air – dried and homogenized soil sample was put into of a soxhlet thimble. The sample was cautiously spiked by adding 1.00 mL of working deuterated surrogate standard solution (i.e., 100 g of deuterated p – terphenyl) to the soil in the thimble. The thimble was then placed in a clean soxhlet funnel. 120 mL of dichloromethane was put into a round bottom flask. The soxhlet apparatus was assembled and the spiked soil sample was extracted for PAHs for 6 hours. The soxhlet apparatus was cooled to room temperature before removing the solvent.

For high level contaminated samples, the solvent was carefully and quantitatively transferred from the round–bottom flask into a stoppered measuring cylinder. The flask was rinsed with 2 mL dichloromethane and added to the content of the measuring cylinder. The contents of the measuring cylinder were thoroughly mixed. 5 mL of this solution was pipetted into 50 mL beaker and 0.5 g of activated alumina was added to it. The content of the beaker was swirled and then allowed to evaporate. A glass – fritted chromatographic column was set up containing activated silica gel to a depth of 60 mm, covered with 0.5 g of activated alumina containing 5 mL of the PAH extract to a depth of 30 mm. the column was conditioned by passing 20 mL of pentane through the column. The pentane eluate was discarded, after which 25 mL of dichloromethane was added to the silica gel column. The eluate was collected and was quantitatively transferred into a rotary evaporation apparatus. The flask was rinsed with 10 mL of dichloromethane and was then added to the soxhlet apparatus. The volume was reduced to 1.0 mL, it was quantitatively transferred to a GC-MS vial. 200 μL of working deuterated p – terphenyl PAH internal standard was added to the GC-MS vial. The vial was sealed tightly with a crimp top for the chromatographic determination of various types of PAHs.

For low level contaminated samples, the solvent in the round – bottom flask was quantitatively transferred into a rotary evaporation apparatus. The flask was rinsed with 2 mL of dichloromethane and the solvent was added to the rotary evaporation apparatus. The contents of the rotary evaporatory were rinsed with 10 mL of dichloromethane and the solvent was added to the beaker. The alumina residue was transferred from the beaker to the top of the column containing the alumina and silica gel and eluted with 20 mL of pentane, the pentane eluate was discarded. A clean rotary evaporation apparatus was placed beneath the column and the PAHs eluted from the column with 25 mL of dichloromethane. The eluate was collected. The extract was rinsed with 2 mL of dichloromethane and then the solvent added to the rotary evaporatory apparatus. The volume was reduced to 1.0 mL, after which the solution was quantitatively transferred to GC – MS vial. 200 μL of working deuterated p – terphenyl standard was used as an internal standard was added to the GC – MS vial. The vial was sealed tightly with crimp top for the chromatographic determination using the GC – MS chromatogram. The efficiency of the solvent extraction process was determined as 67.54%. Recovery and reproducibility studies were conducted. 95.6% recovery was recorded in the recovery and reproducibility studies.

3. Results and Discussion

The results of the various types of PAHs identified from vehicular fallout in Kumasi metropolis and their concentrations have been presented in Table I below.

From Table I, it was realized that 15 different types of PAHs were identified in the fallouts of vehicular movement in Kumasi metropolis. The concentrations of the various types of PAHs identified ranged from 3,500 μg/kg (Carbazole) to 111,200 μg/kg (Acenaphthene).

The concentration of acenaphthene was the highest (i.e., 111,200 μg/kg), suggest that there is high persistence of this type of PAH in the environment. Though health effects of breathing high concentrations of acenaphthene is not known, contact with the skin can cause several disease such as blistering or redness of the skin which may lead to peeling of the skin. Much concerted effort is required to reduce the levels of acenaphthene in Kumasi environment.

Again from Table I, the concentration of bezo[a]pyrene was 27,900 μg/kg. Benzo[a]pyrene is a common PAH and is known to cause lung and skin cancer in laboratory animals. The United States of America Environmental Protection

TABLE I
Mean results of various types of PAHs in vehicular fallouts in Kumasi Metropolis and their concentrations

Compound	Molecular mass (m/e) of analyte	Concentration of analyte (μg/kg)
Naphthalene	128	41,700
Acenaphthylene	152	99,300
Acenaphthene	154	111,200
Fluorene	166	8,900
Carbazole	167	3,500
Phenanthrene	178	12,900
Anthracene	178	5,400
Fluoranthene	202	16,200
Pyrene	202	15,000
Benzo[a]anthracene	228	13,800
Chrysene	228	33,600
Benzo[k]fluoranthene	252	45,700
Benzo[a]pyrene	252	27,900
Perylene	252	57,200
Benzo[g, h, i]perylene	276	47,000

*The calculations were based on the values in appendix I.

Agency (USEPA, 1990) has classified PAHs with benzo[a]pyrene indicator species as a class B 2 pollutant that means a probable human carcinogen with sufficient evidence from animal studies but inadequate evidence from human studies.

The background soil concentrations of PAHs in USA soils set by the Agency for Toxic Substance and Disease Registry have been presented in Table II below.

From Tables I and II, it is clear that benzo [a] pyrene concentration in Kumasi environment is very high. That is, the concentration of benzo[a]pyrene in vehicular fallouts in Kumasi metropolis is higher than the permissible range of background concentration of benzo[a]pyrene in urban soil. It is 169.1 times higher than the background concentration. According to WHO (1987), no safe level can be recommended for benzo[a]pyrene due to its carcinogenicity. Complete removal of PAH from the environment is impossible, but they can be controlled. Therefore standards have to be set for benzo[a]pyrene a known carcinogen in Ghana.

A sample is said to be contaminated if the concentration of the pollutant in the sample is three times higher than the background concentration.

From Table II below, concentrations of acenaphthene, acenapthylene, anthracene, fluorene and phenathrene are not major PAHs pollutant in USA urban soils. This suggests that, these pollutants are not heavily release from vehicular fallouts into the environment. PAHs also occur in the atmosphere in both the particulate phase and the vapour phase. Three–ring PAH compounds are found in the atmosphere primarily in the gaseous phase, whereas, five– and six – ring PAHs are found mainly in the particle phase; four–ring PAH compounds are found in both

TABLE II
Background soil concentrations of polycyclic aromatic hydrocarbons (PAHs) in urban soils

Compound	Concentrations (μg/kg) range
Acenaphthene	–
Acenaphthylene	–
Anthracene	–
Benzo[a]anthracene	169–59,000
Benzo[a]pyrene	165–220
Benzo[b]fluoranthene	15,000–62,000
Benzo[e]pyrene	60–14,000
Benzo[g, h, i]perylene	900–47,000
Benzo[k]fluoranthene	300–26,000
Chrysene	251–640
Fluoranthene	200–166,000
Fluorene	–
Ideno (1, 2, 3-c, d)pyrene	8,000–61,000
Phenathrene	–
Pyrene	145–147,000

phase. To fully characterize atmospheric PAH levels in an urban environment as in Kumasi or cities in USA, both particle – and vapour – phase samples must be collected. The absence of acenaphthene, acenapthylene, fluorene and phenathrene in the USA background urban soil values suggest that, these PAHs because of their low volatility were volatilized quite easily and because only particulate samples were also collected from highways in USA cities, thus no background concentration values recorded in USA urban soils for these PAHs.

However, their presence in urban soil obtained from highways in Kumasi soils calls for more elaborate study to fully understand the mechanism of volatilization of low molecular weight PAHs in an urban environment such as Kumasi.

PAHs can be harmful to health under several circumstances. Several of the PAHs, including benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, and indeno[1,2,3-c,d]pyrene, have caused tumors in laboratory animals when they breathed these substances in the air, when they ate them, or when they had long periods of skin contact with them. Studies of people show that individuals exposed by breathing or skin contact for long periods to mixtures that contain PAHs and other compounds can also develop cancer.

Mice fed with high levels of benzo[a]pyrene during pregnancy had difficulty reproducing and so did their offspring. The offspring of pregnant mice fed with benzo[a]pyrene also showed other harmful effects, such as birth defects and decreased body weight. Similar effects could occur in people, but we have no information to show that these effects do occur (USEPA, 1990).

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 (USEPA, 1990).

4. Conclusion

Concentrations of various types of PAHs have been measured in this study. The results obtained suggest that, the concentration of benzo[a]pyrene a common PAH obtained in this study is higher than the recommended safe limit values set by WHO and the Netherlands ambient air quality standards. Since benzo[a]pyrene is a class B.2 human carcinogen according to USEPA, there is the need to reduce the levels of set safe limit for this pollutant in Ghana, so as to protect road users like drivers, hawkers and other road users in Kumasi metropolis from exposure to toxic effects of benzo[a]pyrene and other PAHs whose health effects are not well known.

It is clear from the results of the study that road users in Kumasi and other major cities in Ghana are exposed to harmful health effects of PAHs in street soil dust. The interesting thing about this study is that most of the vehicles imported into Africa and for that matter Ghana are overage vehicles from Europe and other developed countries, their engines might have run down and therefore releases large amount of toxic pollutants such as PAHs. Much work should be conducted in Ghana to determine the health effects from exposure to PAHs from vehicular movement.

APPENDIX I
Calculation of concentrations of PAHs in the samples

Compound	M/e	Retention time	Peak Area	Response Ratio	Conc. ppm
Naphthalene	128	10.213	253998	0.0072	0.0417
Acenaphylene	152	19.793	150799	0.1246	0.0993
Acenaphthene	154	16.969	122983	0.1016	0.1112
Fluorene	166	18.906	10983	0.0091	0.0089
Carbazole	167	23.503	27859	0.0007	0.0035
Phenanthrene	178	22.625	156072	0.0041	0.0129
Anthracene	178	22.748	51257	0.0013	0.0054
Fluoranthene	202	27.184	17099	0.0052	0.0162
Pyrene	202	27.997	18293	0.0056	0.0150
Benzo [a]anthracene	228	32.731	12851	0.0039	0.0138
Chrysene	228	32.880	24594	0.0075	0.0336
Benzo[k]fluoranthene	252	36.682	48422	0.0151	0.0457
Benzo[a]pyrene	252	37.720	14766	0.0046	0.0279
Perylene	252	38.003	49458	0.0154	0.0572
Benzo[g,h,I]perylene	276	41.947	69433	0.0216	0.0470

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