

SHORT COMMUNICATION

POLYCYCLIC AROMATIC HYDROCARBONS IN MUNICIPAL WASTE ASHES FROM THREE WASTE DUMPS IN LAGOS, NIGERIA

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(Received August 28, 2004; revised December 13, 2006)

ABSTRACT. The levels of isolated polycyclic aromatic hydrocarbons (PAH) in ash residues of wastes from some major waste dumps in Lagos, Nigeria, were determined. The total amounts of the PAH in the ashes were in the range of 0.06 – 0.4 µg/g. The ash from the waste dump that contains the highest level also displayed greatest variety of PAH.

KEY WORDS: Polycyclic aromatic hydrocarbons (PAH), Ashes; Waste dumps; Lagos - Nigeria

INTRODUCTION

In Lagos, Nigeria, wastes disposal systems are not effective as the inhabitants and some industries choose to dispose their wastes indiscriminately around the city. Despite the Federal Environmental Protection Agency's (FEPA) law that prohibits this act, indiscriminate disposal of wastes never ceases. Either, accidentally or intentionally the wastes are set on fire resulting in continuous production of smoke from the waste dumps.

Polycyclic aromatic hydrocarbons (PAH) are compounds with two or more benzene rings that have long polluted the environment and food. PAH are introduced into the environment by the incomplete combustion of fossil fuels and other organic materials from industrial processes, forest fires and oil spills [1]. Another source of these compounds, some of which have been found to be carcinogenic and/or mutagenic, is refuse burning [2-6].

In the last decade (1990's), there have been several data on concentrations of toxic pollutants from many industrialized countries. However, in developing countries, information is scarce on PAH and other trace organic compounds resulting from burning of refuse. Some studies have provided analytical data for PAH sludge ash [6] and ash residues [7-8] from incinerators combusting raw municipal refuse. The potential health hazards associated with refuse dumps underscore the need to monitor waste effluents resulting from burning of the refuse. The effluents may be rich in PAH, some of which are potent carcinogens. It is important to know the toxicant loadings in this ash because it may be leached into ground waters since it is often disposed off in landfills, also, it may be used as an amendment to agricultural soils where accumulation and uptake of PAH by crop may occur. Leung *et al.* [9] reported environmental contamination caused by recycling of electronic waste. A 0.59 µg/g of polycyclic aromatic hydrocarbons at the dump site was reported. Enrichment of polycyclic aromatic hydrocarbons in forest soil near a blast furnace plant was reported by van Brummelen *et al.* [10]. In their studies, Hayakawa *et al.* [11] reported high concentration of polycyclic aromatic hydrocarbons in the atmosphere and bulk deposition in Kyoto, Japan.

This study is aimed at identifying the sources and quantifying the pollution levels generated from the studied waste dumps at Lagos, Nigeria, and their potential impacts on the environment and human health.

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EXPERIMENTAL

Refuse was collected from three major waste dumps located at Ojota, Aboru and Ipaja. The wastes were incinerated at 900 °C. The ashes were air-dried, pulverized, separated with a 3 mm sieve, mixed thoroughly and stored at room temperature. A 50 g of ash sample from each of the three refuse dump sites were weighed and spiked with pre-deuterated PAH Cocktail as internal standard (IS) mixture acenaphthalene-d₁₀, phenanthrene-d₁₀ and crysene-d₁₀ (Supelco, USA), and then extracted in a Soxhlet extractor for 8 h with 300 mL of 1:1 benzene: methanol. A 10 g of the crude extract were adsorbed onto 100 g silica gel (Fisher Scientific, 28 - 200 mesh) which had been washed with methylene chloride and activated at 260 °C. Samples and solutions were protected from light during extraction and isolation.

Benzene, toluene, methylene chloride and hexane were A.C.S. certified (Fisher Scientific, Fairlawn, New Jersey). PAH were isolated in the methylene chloride fraction eluted in the final silica gel chromatographic steps for each extract. These fractions were carefully evaporated at 30 °C and 1 mL of toluene was added immediately. The toluene-soluble portion of the PAH was analyzed using fused silica capillary gas chromatography with mass selective detector (MSD) and combined gas chromatography-mass spectrometry. The fractions were chromatographed on a Varian 3700 GC which was fitted with Hewlett-Packard (HP) SE 54 fused silica capillary column (18 m x 0.2 mm i.d.) to obtain quantitative data for major PAH compounds. The carrier gas was helium at a linear velocity of 36 cm.s⁻¹. Detector and injector temperatures were maintained at 300 °C and 250 °C, respectively.

Various isothermal column oven temperature ranging from 180 to 230 °C at 3 °C min⁻¹ were used for each isolated sample to resolve individual PAH from other sample components and possible isomers over a relatively wide range of molecular weight (150-300). The PAH were identified by comparison of retention data with those of standard compounds (PAH standards Kit plus triphenylene) obtained from Analabs, Incorporation (North Haven, California).

A modified Varian 3700 GC fitted with a HP SE 54 fused silica capillary column (15 m x 0.2 mm i.d.) and connected to a Varian MAT 112 S mass spectrometer (electron energy 70 eV, filament current 7 µA), the oven temperature programmed from 150 °C to 300 °C at 3 °C min⁻¹ using helium as carrier gas at the flow rate of 2 mL min⁻¹ was used to obtain electron impact (EI) spectra for the detection of the most abundant PAH species, and negative chemical ionization (NCI) mode for the detection of highly sensitive compounds, that capture electrons.

RESULTS AND DISCUSSION

Table 1 lists the concentrations of phenanthrene, anthracene and fluoranthene in the refuse ashes of the three sites under study. The accuracy of the method was assessed by recovery experiments in which several PAH standards were carried through the isolation procedure. The results of the PAH standards, PAH recoveries and percentage recoveries are given in Table 2. In all the cases, recoveries of PAH were greater than 70 %.

Table 1. Phenanthrene, anthracene and fluoranthene in the refuse ashes location.

Location	Concentration (ng/g)		
	Phenanthrene	Anthracene	Fluoranthene
Aboru	360	315	385
Ojota	93	80	110
Ipaja	85	60	90

Table 2. Mean levels of PAH in PAH standards and their recoveries.

PAH	Level of PAH ($\mu\text{g/g}$)	Recoveries ($\mu\text{g/g}$)	% Recoveries
Phenanthrene	10.3 \pm 0.2	8.2	80
Anthracene	6.0 \pm 0.2	4.7	78
Fluoranthene	6.9 \pm 0.3	6.4	78
Pyrene	6.5 \pm 0.4	5.2	80
1,2-benzanthracene	5.8 \pm ns	3.6	62
Dibenzothiophene	5.2 \pm 0.1	4.6	88
Methylanthracenes/-phenanthrene	9.4 \pm 0.6	6.5	69
Methyldibenzothiophenes	2.3 \pm 0.2	1.7	74
Ethylanthracene/-phenanthrene	5.1 \pm 0.2	4.2	82
Ethylidibenzothiophenes	3.4 \pm 0.1	2.3	68
Methylfluoranthenes or methylpyrene	4.5 \pm 0.3	3.4	76
Benzo [ghi] fluoranthene	6.4 \pm 0.2	4.9	64
Benzopyrenes or benzofluoranthenes or perylene	4.0 \pm 0.2	2.5	63

ns = not significant.

A procedure blank which included extraction and isolation steps were prepared and run with GCMS, chromatogram shows no peaks interfering with the determination of compounds of interest. The limit of detection of mass selective GC used for quantifying the PAH studied was approximately 50 $\mu\text{g/g}$ of ash and 25 $\mu\text{g/g}$ of ash for GCMS.

Because of the stability of their aromatic ring systems, the individual PAH have simple mass spectrum which exhibits little fragmentation and the molecular ion is the base peak in every case. This characteristic is a sensitive indicator of the compound class; however, it does not allow for a distinction between PAH isomers. Therefore, a combination of gas chromatographic retention time of resolved species together with the individual mass spectrum is required for identification. Quantitative data for resolved PAH isomers were obtained by isothermal mass selective gas chromatography (Table 3).

Table 3. PAH levels in Aboru waste ash.

PAH species	Concentration (ng/g)
Phenanthrene (178)	360
Anthracene (178)	315
Dibenzothiophene (184)	105
Methylanthracenes/ -phenanthrene (192)	240
Methyldibenzothiophenes (198)	65
Fluoranthene (202)	385
Pyrene (202)	313
Ethylanthracene - phenanthrene (206)	120
Ethylidibenzothiophenes (212)	95
Methylfluoranthenes or methylpyrene (216)	60
Benzo [ghi] fluoranthene (226)	98
1,2-benzanthracene (228)	99
Benzopyrenes or benzofluoranthenes or perylene (252)	78

Values in parentheses are the molecular weight of individual PAH species.

The gas chromatograph traces of final fractions isolated from the three waste ashes showed that more PAH were present in the Aboru waste dump than in the other two ashes where anthracene, phenanthrene and fluoranthene were found at measurable levels (Table 1).

The GCMS data were searched for the molecular ions of commonly occurring PAH and their alkylated homologs. The Aboru waste ash contained a variety of PAH species (Table 3).

Electron impact GCMS was used to examine the most abundant of the PAH species. Phenanthrene (m/z 177), anthracene (m/z 178), fluoranthene (m/z 202), pyrene (m/z 202) and methylanthracene or methylphenanthrene (m/z 192) were detected. The final fraction isolated from the Aboru waste ash was further examined using GCMS under electron capture negative chemical ionization conditions and PAH of molecular weight 276, 278 and 300 were detected. The negative chemical ionization technique allows greater sensitivity than the electrons impact mode. Furthermore, there was an ionization discrimination enhancing the intensity of species at higher mass relative to electron impact data for the same mixture. This is particularly evident for the PAH at m/z 252, 276, 278 and 300. There are several possible isomers at m/z 276 including benzofluoranthene and benzo [ghi] perylene; m/z 278 and m/z 300 are probably dibenzanthracene and coronene, respectively.

The distribution of PAH observed on the Aboru waste ash is consistent with their formation at a temperature of about 900 °C or higher. PAH that bear no alkyl side chain or only methyl-predominate in this temperature range [12-15].

Conclusively, there is correlation between the levels of PAH and the anthropogenic input into the waste dumps studied. Levels of some of the PAH in the dump sites were higher than the guidelines of Canadian Environmental Quality of 0.02 µg/g.

ACKNOWLEDGEMENTS

The authors acknowledge the management and staff of Chevron Central Laboratory, Lagos, for the permission to use GCMS instruments. Also, the effort of our student O. Shareefah during the sampling is acknowledged.

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