Polycyclic aromatic hydrocarbons in urban air: concentration levels and patterns and source analysis in Nairobi, Kenya

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) present in the environment are mainly due to incomplete combustion of organic matter. They are widely distributed ubiquitous environmental pollutants, and a number of PAHs especially high molecular weight are known carcinogens, mutagens and some are suspected to be endocrine disrupters[1]. Certain PAH concentration ratios to benzo[e]pyrene have been used to differentiate PAH sources sucessfully[2, 3]. Due to the stability and health concerns of particle bound PAH, only samples collected using quartz filter papers were analyzed. Our aim for the present work was to report the concentration levels and patterns of these PAH including the higher molecular weight fractions which are potentially toxic and lacking in many PAH researched studies. We, therefore, analyzed daily air samples collected for thirty different PAHs in three different sites covering residential, industrial and central business district during the period of 25th August to 12th September 2003 in Nairobi, Kenya. To the best of our knowledge, no or little data is available on PAH levels in Nairobi.
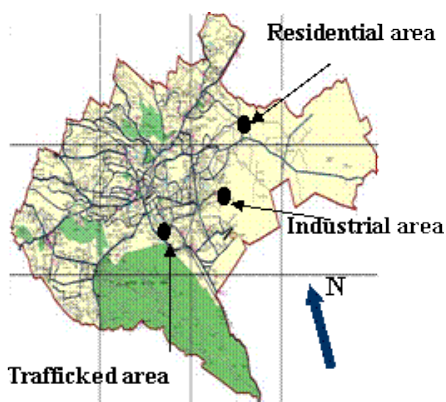
Materials and Methods

Fig. 1. Sampling sites in the city of Nairobi, Kenya

Sampling sites were located in trafficked, industrial and residential areas in Nairobi, Kenya (Fig. 1). Air samples were collected on quartz filters using a mini-pump (Sibata, Tokyo, Japan) at 5 L·min^{-1} from the three different areas. Among the total of 24 samples, the volumes of air collected ranged from 0.47 to 0.93 m^3. The quartz filters samples were folded and stored in aluminum foil under 4 °C until analysis.

PAH analysis was adapted from previously published methods[4, 5]. Briefly the filter samples were spiked with 100 µl of 1.25 µg/ml of deuterated PAH and extracted by an automated Soxhlet equipment (Soxtherm, Gerhardt, Germany) using a 1:1 mixture of acetone:hexane solution (140 ml) at 140 °C for 2 hrs and 31 minutes. The extract was cleaned up by a Sep-Pak silica cartridge (Waters, Massachusetts, USA) with 10-12 ml of 20% acetone:hexane mixture. This was then concentrated to 0.9 ml by N$_2$ purge at room temperature and 100 µl of 1 µg/ml internal standard (pyrene-d$_{10}$) was added in to the vial. The sample was then stored in the freezer below 4 °C until analysis with GC-MS. Two µl of the extracted sample in the vial was injected a GC-MS (Agilent HP6890 series GG and HP5973 series MS) equipped with a DB-5 capillary column (60 m x 0.25 mm i.d.; 2.5 µm film thickness, J&W Scientific, Folsom, CA) and detected by selected ion monitoring mode. Internal standards method and Agilent special programs such as retention time locking, chemstation program and NIST library were used to determine PAH concentration in the samples.

Statistical analysis was performed using statistical software (StatSoft Inc, Tulsa, USA). PAH concentration levels were reported for their average, median, standard deviation, range, and Pearson's correlation coefficients. The data was analyzed for sources by principal component analysis (PCA) and isomer ratio analysis. Nonparametric tests like Kruskal-Wallis test were used to detect inherent differences in PAH concentration data obtained from different sites.

Results and Discussion

Table 1 gives a summary of higher molecular weight PAH concentrations in Nairobi for all the sites sampled. Results indicated that pyrene was the most abundant PAH with concentration range of 0.5 and 46.0 ng/m^3. Concentrations of carcinogenic PAHs like benzo[a]pyrene, benzo[k]fluoranthene, dibenzo[a,h]anthracene, indeno[1,2,3-cd]pyrene, dibenzo[a,e]pyrene, and dibenzo[a,l]pyrene, were higher in trafficked areas but less in residential areas. Consistent with previous research, benzo[ghi]pyrene, coronene, and indeno[1,2,3-cd]pyrene were more abundant in trafficked areas. Generally, 5- and 6-ring PAHs were more abundant in trafficked areas (55%), while 3- and 4-ring PAHs were mostly found in the residential areas (60%).

Table 1. Concentrations of higher molecular weight PAHs (ng/m^3) in Nairobi, Kenya.

PAHs	Trafficked area (n = 10) Range	Median	Industrial area (n = 8) Range	Median	Residential area (n = 6) Range	Median
Fth	0.2 - 17.8	11.4	0.4 - 26.7	6.8	0.4 - 20.3	12.0
Py	0.8 - 34.0	18.2	0.5 - 46.0	11.0	4.8 - 28.2	18.9
B[a]A	2.3 - 15.3	11.8	2.6 - 15.2	5.7	5.0 - 19.6	8.8
Chy	1.9 - 18.4	12.8	3.7 - 20.4	7.6	4.7 - 20.5	10.9
B[b]Fth	1.2 - 22.9	6.8	1.7 - 17.9	5.9	3.1 - 11.0	4.7
B[j+k]Fth	1.0 - 11.0	5.0	1.4 - 15.2	4.8	2.6 - 9.4	4.1
B[e]P	1.8 - 17.9	11.6	4.1 - 18.4	8.9	4.7 - 9.1	6.5
B[a]P	1.3 - 24.7	17.0	2.1 - 21.3	11.4	3.2 - 16.4	11.4
IP	2.2 - 18.6	10.8	4.0 - 16.7	7.3	5.4 - 7.5	6.5
Db[a,h]A	0.1 - 8.0	0.9	0.3 - 5.1	0.9	0.1 - 2.8	1.2
B[ghi]P	2.7 - 40.8	27.5	8.9 - 42.3	15.5	7.3 - 13.0	8.8
Db[a,l]P	0.2 - 3.1	0.7	0.5 - 4.4	0.9	0.6 - 3.0	1.2
Db[a,e]P	0.7 - 9.4	2.1	0.0 - 6.3	1.3	0.8 - 4.1	1.3
Cor	1.3 - 25.3	15.4	1.4 - 10.6	7.1	0.3 - 7.1	3.8

The correlation coefficient between coronene and benzo[ghi]perylene was high (R=0.94, n=10) in the trafficked area suggesting diesel and gasoline engine emissons as probable PAH sources[6]. High correlation between benzo[c]phenanthrene and 3,6-dimethyl phenanthrene (R=0.98, n=8) for industrial area samples indicated that industrial oil combustion was the major source[6]. For residential area samples, correlation between flouranthene and pyrene (R=0.97 n=6) suggested PAHs could be due to domestic fuel (wood burning)[7]. PAH isomer ratio analysis showed that PAH from Nairobi is mainly from traffic emissons (gasoline and diesel cars) and probably oil combustion (Table 2). Considering the ratio for coronene/benzo[e]pyrne (Cor/B[e]P), low values recorded in residential area (0.62) and industrial area (0.84) relative to trafficked area (1.18). This was due to high concentration of B[e]P relative to Cor in these areas, suggesting other sources other than traffic influence PAH in these areas. A ratio of 1.8 attributable to traffic emissions was recorded in previous research[7]. This value is greater than the one reported in this study. The isomer ratios recorded in this study were comparable to those reported in a study carried out in Greece[8].

Table 2. Summary of isomer ratios of selected PAHs

Isomer ratios	TA		IA		RA	
	Range	Average	Range	Average	Range	Average
Fth/(Fth + Py)	0.06-0.95	0.36	0.06-0.91	0.38	0.08-0.42	0.34
B[a]A/Chry	0.60-1.21	0.97	0.55-1.21	0.72	0.66-1.21	0.97
B[a]A/(B[a]A +Chry)	0.38-0.55	0.48	0.35-0.55	0.41	0.40-0.55	0.49
B[e]P/(B[e]P+B[a]P)	0.38-0.61	0.46	0.33-0.69	0.51	0.30-0.63	0.45
B[ghi]P/B[a]P	1.10-2.70	1.80	0.81-4.31	2.23	0.45-3.70	1.49
IP/(IP+B[e]P)	0.39-0.58	0.49	0.42-0.50	0.46	0.41-0.56	0.49
Cor/B[e]P	0.63-1.56	1.18	0.07-1.19	0.84	0.03-1.18	0.62
IP/(IP+B[ghi]P)	0.23-0.46	0.33	0.27-0.43	0.32	0.33-0.51	0.41

TA = Traffic Area, IA = Industrial Area, RA = Residential Area

Principal component analysis with varimax rotation was carried out on the data to determine inherent differences and sources of PAH. The first five principal components accounted for 64% of the variance. The first principal component accounting for 19% of the variance had a high positive loading for benzo[e]pyrene (0.87), benzo[ghi]perylene (0.81) and coronene (0.65) this principal is attributable to traffic emissions. The second principal component had a high positive loading for 3, 6-dimethyl phenanthrene (0.75), benzo[c]phenanthrene (0.77), dibenz[a,h]pyrene (0.84) and dibenzo[a,e]pyrene (0.91) this was interpreted as oil combustion [6]. Principal component scores for the sampling areas were not well separated this could be due to mixing of PAH from the diffrent sources.

Statistical analysis showed no significant differences between the sampling areas for 3- ring (Kruskal-Wallis, H = 1.41, df = 2, p < 0.05), 4- ring (Kruskal-Wallis, H = 3.25, df = 2, p < 0.05), 5-ring (Kruskal-Wallis, H = 0.245, df = 2, p < 0.05) and 6-ring PAHs (Kruskal-Wallis, H = 6.1, df = 2, p < 0.05). Significant differences were observed for the 6-ring PAHs (Kruskal-Wallis, H = 6.1, df = 2, p < 0.01). This difference could be partly due to the fact that 6- & 7- ring PAHs are mainly found in trafficked areas than in other areas sampled. Generally PAH profiles were not well separeted for the Nairobi air samples collected. Further source distinction, needs more data sets (over 50 samples) and better models like positive matrix factorization (PMF)[9] which have been used successfully to apportion sources of pollutants.

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