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Research Article

# ESTIMATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) POLLUTANTS IN THE AMBIENT AIR OF KHARTOUM CITY, SUDAN (Part III)

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**ABSTRACT**

Atmospheric concentration levels and percentage (%) composition of fourteen Polycyclic Aromatic Hydrocarbons (PAHs) were estimated in air samples collected by High-Volume Air Sampler TE-1000 PUF and determined via Gas Chromatography Mass Spectrometer GC/MS at an urban site of Khartoum City, Sudan. The results for a given air sample are presented as the sum of the vapor and particle associated fraction of the compounds. The percentage composition of individual PAHs in the air sample in (ng/m$^3$) is found to be as follows: phenanthrene (33%,14.3ng/m$^3$), fluoranthene (16%,7.8ng/m$^3$), pyrene (15%,6.6ng/m$^3$), anthracene (4%,4ng/m$^3$), chrysene (8%,3.5ng/m$^3$), benzo(a)pyrene (5%,2.6ng/m$^3$), benzo(a)anthracene (3%,2ng/m$^3$), benzo(b+k)fluoranthene (6%,1.7ng/m$^3$), fluorine (3%,1.5ng/m$^3$), benzo(g,h,i)perylene (2%,1.3ng/m$^3$), indeno(1,2,3-cd)pyrene (2%,1.1ng/m$^3$), acenaphthene (2.5%,1ng/m$^3$) and dibenzo(a,h)anthracene (1%,0.3ng/m$^3$), respectively. PAHs concentrations showed slight variation in concentrations in air mass flow from NE or SW due to the invariability of temperature during the sampling. For all of the detected PAHspollutants benzo(a)pyrene B(a)P is detected in all the collected samples.

**Keywords:** Ambient Air; TE-1000 PUF Sampler; GC.MS; PAHs; concentration levels; % Composition.

## 1. INTRODUCTION

Polycyclic Aromatic hydrocarbons (PAHs) are a class of genotoxic environmental contaminants[1-6].They are produced in all processes of incomplete combustion of different kinds of fuels and organic substances [7].PAHs entering the atmosphere derived from the combustion and from volatilization are present in the ambient air as vapors or adsorbed into airborne particulate matter[8,9]. PAHs have received increased attention in research studies of air pollution in the past two decades, because some of them are known to be highly carcinogenic or mutagenic[10]. The high carcinogenicity and mutagenicity of some are well documented in the literature, e.g. benzo(a)pyrene[11-16], yet no research investigations have been conducted prior to this current study in the Sudan. The present research paper describes the establishment of the sampling procedure, extraction method and a record of validation of GC/MS analytical technique for the estimation of the levels of PAHs in the ambient air of Khartoum City. The general aim is to extend the investigation to include other urban areas in the Sudan. The current study is an extension to our previous reported investigations of exposure of the population of Khartoum to hazardous air pollutants[17,18].

## 2. EXPERIMENTAL

### Sampling Procedure

An air sample is collected directly from the ambient atmosphere using high volume air sampler (TE-1000 PUF Sampler, Tischenv.), (Correlation coefficient=0.9944; Sampler Set Point = (0.246m$^3$/min). Sampling time may be

varied from 9 to 24 h, so as not to exceed a total volume of 350 $m^{319}$.
Quartz fiber filters (104-mm, binderless) and PUF (polyether type, density 22 $mg/cm^3$) were pre-cleaned (QFF: heating in oven at 450 °C for 8 hr, PUF: extracted in Soxhlet extraction assembly with Acetone for 14-24 h at 4cycles per hrs). Thirty samples were collected from one site in Khartoum State. Twenty of these samples were collected over the truly period. Given that the remaining ten samples were unvalid due ,leakages of the collected of the polluted air .

**Sampling Sites**
In this study, air samples were collected in Alhilla Al-Jadeda west Khartoum city which represents a typical urban site. The collection site is surrounded by an incineration site, adomestic heating activities using natural gas (bakeries), heavy traffic roads and car-repair garages Figure 1.

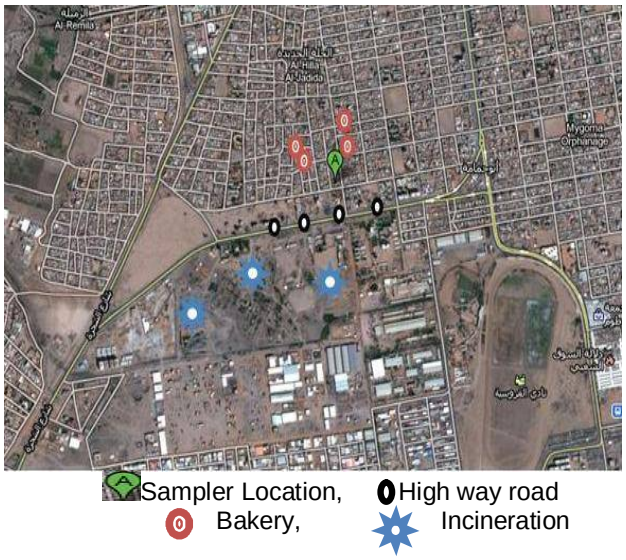



**Fig. 1: Air sampling Points in AlhillaAljadida-Khartoum City**

**Extraction Procedure**
The particulate filter and sorbent cartridge are extracted together in Soxhelt Extractor (300 ml, 10% diethyl ether in hexane). The sample extract is concentrated by a Kuderna-Danish concentrator, and a fractionated through Silica Gel Column, prior to analysis. The diethyl ether/hexane fraction was collected, concentrated to 1 ml and then finallyinternal standards were added to the concentrate.

**Establishment of the Analytical Technique**
The PAHs were identified using a GC chromatograph coupled to a mass spectrometry detector (Shimadzu model GCMS-QP2010) and a NIST library. The detection mode used for identification was: single ion monitoring (SIM). A 30-m fused-silica capillary column, RTX- 5MS (0.25mm ID, 0.5 mm film thickness). Theoven temperature programs50 °C (0.8 min), 30 °C /min to 290 °C (0 min), 4 °C /min to 315 °C (0 min), 2 °C /min to 320 °C (3 min) were used for separation identification and estimation of the PAHs pollutants

The components of the standard PAH mixture were:naphthalene-$d_8$ ISs, naphthalene, acenaphthene-$d_{10}$ ISs, acenaphthene, fluorine,phenanthrene-$d_{10}$ ISs, phenanthrene, anthracene**,** fluoranthene**,** pyrene, benzo(a)anthracene, chrysene-$d_{12}$ ISs, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, perylene-$d_{12}$ ISs, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i) perylene (Accustandard Co.). This standard mixturewas used for the determination of the retention time of the peaks of individual PAH-components and for their quantification asinternal standards in comparison with those PAHs-components in the collected air polluted samples at the same GC-conditions..

## 3. RESULTS AND DISCUSSION

**Data and Procedure Validation**
The GC.MS system was set-up in the mass spectral ion abundance criteria 83.3% by instrument performance check solution containing DFTPP, Table 1. DFTPP was used to meet CLP Criteria for PAHs GC-MS-analysis.

**Table 1: DFTPP used to meet CLP Criteria for PAHs Analysis**

| Data | Data File Path | Sample Name | Sample ID |
|---|---|---|---|
| Data1: | F:\PDFTPP\DFTPP day3.QGD | DFTPP day3 | Check |
| Dftpp: | Analysis Date: 11/8/2010 | | |
| M/Z | Spectrum Check Criteria | Relative Abundance | Status |
| 51 | 30-60 percent of mass 198 | 41.174503 | Pass |
| 68 | Less than 2 percent of mass 69 | 1.448052 | Pass |
| 70 | Less than 2 percent of mass 69 | 0.519171 | Pass |
| 127 | 40-60 percent of mass 198 | 56.727526 | Pass |
| 197 | Less than 1 percent of mass 198 | 0.597896 | Pass |
| 198 | Base pake,100 percent relative abundance | 100.0000 | Pass |
| 199 | 5-9 percent of mass 198 | 6.878461 | Pass |
| 275 | 10-30 percent of mass 198 | 29.030856 | Pass |
| 365 | Greater than 1 percent of mass 198 | 2.895576 | Pass |
| 441 | Percent but less than mass 443 | - | Fail |
| 442 | Greater than 40 percent of mass 198 | 0.0000 | Fail |
| 443 | 17-23 percent of mass 442 | - | Pass |

**Table 2: shows the correlation coefficient, $R^2$, the relative standard deviations %RSD, which were both obtained from Initial Calibration Curves of the targetedPAHs.It could be noticed that the relative standard deviations were < 20% for most PAHs except for naphthalene , which has an extremely high value of 43%. Limits of quantitation (LOQs) were estimated on the signal observed at the lowest point of the calibration curve. The precision were ≤ 0.005ng/µL for most PAHs, except for indeno(1,2,3-c,d)pyrene, dibenz(a,h)anthracene, and benzo(g,h,i)perylene compounds (The precision was found in the range between 0.02 to 0.1ng/µL). The linearity was assessed on three calibration levels for each analyte (pollutant) over the respective range of (0.1–2.5) ng/µL. Correlation Coefficient ($R^2$) was better than 0.998 for all analytes.**

**Table 2: calculated $r^2$ and % RSD from Initial Calibration of the PAHs Standards**

| PAHs | $R^2$ | %RSD |
|---|---|---|
| Naphthalene | 0.99976 | 43 |
| Acenaphthene | 0.99973 | 18 |
| Fluorene | 0.99986 | 16 |
| Phenanthrene | 0.99997 | 19 |
| Anthracene | 0.99997 | 17 |
| Fluoranthene | 0.99999 | 13 |
| Pyrene | 0.99993 | 14 |
| Benzo(a)anthracene | 0.99969 | 20 |
| Chrysene | 0.99967 | 20 |
| Benzo(b)fluoranthene | 0.99953 | 23 |
| Benzo(k)fluoranthene | 0.99972 | 20 |
| Benzo(a)pyrene | 0.99984 | 14 |
| Indeno(1,2,3-c,d)pyrene | 0.99963 | 12 |
| Dibenz(a,h)anthracene | 0.99866 | 19 |
| Benzo(g,h,i)perylene | 0.99972 | 7 |

**Estimation of total PAHs in the ambient air of Khartoum City**

As the percentage relative standard deviation (%RSD) for naphthalene is over the expected value (43%), then its estimation value was rejected (i.e. %RSD is > 20%). Benzo(b)fluoranthene and benzo(k)fluoranthene peaks are not well resolved in the sample chromatograms, accordingly, were integrated together and reported as a sum.

**Table 3: Estimation of the percentage Composition of PAHs in polluted air samples**

| PAHs | ng/m$^3$ | % |
|---|---|---|
| Phenanthrene | 14.3 | 33.0 |
| Fluoranthene | 7.8 | 16.0 |
| Pyrene | 6.6 | 15.0 |
| Anthracene | 4.0 | 4.0 |
| Chrysene | 3.5 | 8.0 |
| Benzo(a)pyrene | 2.6 | 5.0 |
| Benzo(a)anthracene | 2.0 | 3.0 |
| Benzo[b+k]fluoranthne | 1.7 | 6.0 |
| Fluorene | 1.5 | 3.0 |
| Benzo(g,h,i)perylene | 1.3 | 2.0 |
| Indeno(1,2,3-c,d)pyrene | 1.1 | 2.0 |
| Acenaphthene | 1.0 | 2.5 |
| Dibenz(a,h)anthracene | 0.3 | 2.0 |

The light PAHs component phenanthrene has shown the highest level of concentration (33%) in addition to its frequent detection in all air samples. Such regular frequencies of detection and uniform high level of concentration level indicates that the abundance of the lighter PAHs are consistent with their being used in polyurethane foam (PUF) industry prevailing around the site of sampling. The lowest frequency of detection of all of the PAHs pollutants was for dibenz(a,h)anthracene, which was detected in not more than 1%. The most important PAH-pollutant, benzo(a)pyrene (BaP) was detected in 5%. Alone, such percentage will, probably, underestimate the carcinogenic potential of airborne PAH mixtures) (19-24),

**Statistical analysis of the PAHs pollutants based on Wind Directions**

Measurement of wind speed and wind direction is important in air monitoring. It can help to identify: The location of the pollution sources and what is happening in the air. Wind patterns were classified according to wind directions mainly from NE (north east), and SW (south west). The statistical package for social science (SPSS) was adopted, T. test was used for comparison of the results. The result is significant when the P. value is less than 0.05.

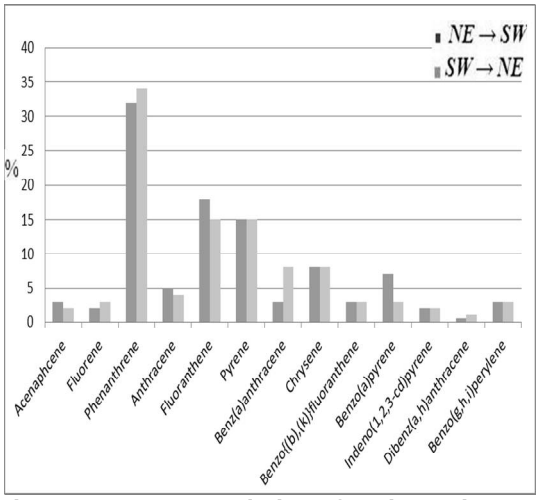
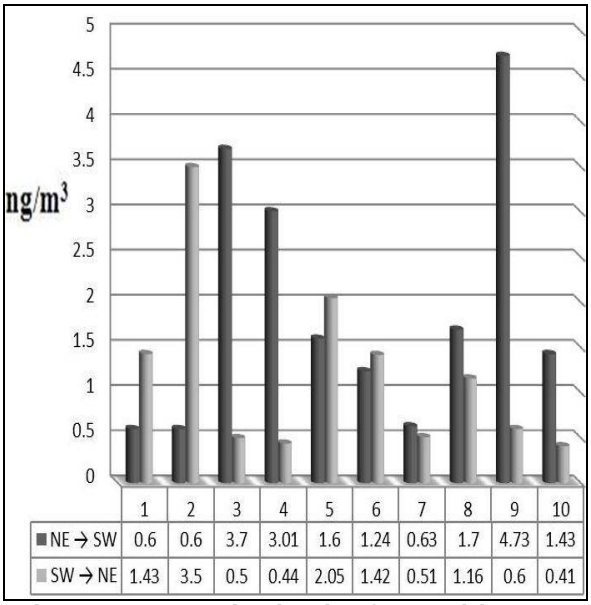



**Fig. 2: Summary Statistics of Estimated PAHs**

Figure (2) is showing that SW wind directions contribute more than 57 % of the total for most the PAHs air pollutants. The highest average concentration levels were obtained for: phenanthrene (14.3ng/$m^3$), fluoranthene (7.8ng/$m^3$), pyrene (6.6ng/$m^3$), anthracene(4ng/$m^3$), chrysene (3.5ng/$m^3$), and benzo(a)pyrene (2.6ng/$m^3$).

**Levels of Benzo(a)Pyrene air pollutant**

Literature contains no specific monitoring guidelines for the values of the levels of PAHs pollutants in the embient air or any minimal level of exposure. The UK and the EC recommend that benzo(a)pyrene (BaP) monitoring levels could be taken as a substitute for the total abundance of PAHs in the ambient air[25]. It is noteworthy to mention that the metabolites of benzo(a)pyrene (BaP are mutagenic and highly carcinogenic, and it is listed as a Group 1 carcinogen by the IARC[12].




| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| NE → SW | 0.6 | 0.6 | 3.7 | 3.01 | 1.6 | 1.24 | 0.63 | 1.7 | 4.73 | 1.43 |
| SW → NE | 1.43 | 3.5 | 0.5 | 0.44 | 2.05 | 1.42 | 0.51 | 1.16 | 0.6 | 0.41 |

**Fig. 3: Concentration levels of Benzo(a)Pyrene Relative to Wind Directions**.

**CONCLUSIONS**

An appropriate air sampling procedure, an efficient extraction of pollutants from air samples has been established. Some of the validation parameters of the analytical GC-MS-method for the estimation of PAHs were checked and determined.

The identification and estimation of the levels of PAH-pollutants in the environment of Khartoum city provides a description of the current environmental situation, in respective, to one of the most important group of volatile aromatic hydrocarbons species. Although caution is needed when analyzing the results owing to the small number of samples, and also to the climatic factors that should be taken into consideration.

There is slight variation in concentrationlevels in air mass flow from NE or SW, which is, likely, due to UN high change in temperature during sampling.

It is noteworthy to record that the average concentration, and accordingly, the exposure level of BaP varied, relative to wind directions, namely, which was between (0.6-4.7ng/$m^3$) and (0.4-2.05ng/$m^3$) NE and SW air directions, respectively.

The sources of emission of PAH-pollutants in the ambient air of Khartoum City are apparently, primarily from bakeries, then vehicles exhausts due to heavy traffic and moreover due to the incineration practices nearby residential areas.

**Recommendations**

It is now feasible to carry out a short or long-pilot survey for the estimation of PAHs pollutants in the ambient air of Khartoum and other cities in the Sudan. The diameter of the sampling site should lengthen to include Greater Khartoum. Long term pilot research studies should be conducted during all durations of the day and through all the seasons of the year.

Government legislations should be issued by the appropriate local authorities for the

prohibition of some human practices that contribute in air pollution. Correlation studies between the PAHs-pollutants and their negative health impacts should be conducted.

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