Risk Assessment of Poly Cyclic Aromatic Hydrocarbons in the Holy City of Makkah, Saudi Arabia

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Abstract—There is a lack of information on polycyclic aromatic hydrocarbons (PAHs) as environmental pollutants in Saudi Arabia. The current study focuses on the risk assessment of polycyclic aromatic hydrocarbons (PAHs) in the Holy city of Makkah, Saudi Arabia, during Hajj season 1431H. Atmospheric particulate matter was collected using High Volume samplers. Samples of 24h were collected at three sampling sites, Al-Shebakah, Al-Aziziah and Mina. PAH compounds were quantified by using GC. The total PAH concentrations (ng/m^3) ranged from 103.5 - 195.2 with mean values of 164.67, 137.81 and 132.40 for TSP, PM_{10} , $\text{PM}_{2.5}$, respectively. The higher percentages of the total carcinogenic compounds were recorded at Al-Shebakah, with a maximum value of 63.5 % in PM_{10} . The carcinogenic PAHs, dibenzo[a]pyrene was found at low concentrations.

Index Terms—Polycyclic aromatic hydrocarbons, risk assessment, makkah.

I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are widely distributed as environmental pollutants and have both anthropogenic and natural sources [1]. PAHs are semi-volatile organic compounds, and present in both gaseous and particulate phases. The partitioning of PAH compounds between the particulate and gaseous phases depends on the atmospheric conditions, the nature of aerosol, the interactions between the compound and the aerosol, and the overall behavior of the compound in the atmosphere [2].

PAHs are generated through the combustion of fossil fuel and biomass. Combustion sources include automobiles, power plants, industries, burning coal and petroleum, and waste incinerators. In urban and industrial areas, atmospheric PAHs are almost entirely anthropogenic in origin and are produced by high-temperature reactions, such as incomplete combustion and pyrolysis of fossil fuels and other organic materials containing carbon and hydrogen [3]. The major sources of PAHs in urban atmosphere are gasoline and diesel vehicle exhausts, tire wear debris, asphalt particles, re-suspended soils, and power plants [3]. Natural emission sources of PAHs include forest fires and volcanoes.

PAHs have been identified to be one of the major toxic air pollutants, and some of their degradation products have been known as carcinogenic, mutagenic, and allergenic agents to human health [1]. Many studies have focused on PAHs levels, and distribution in suspended particulate matter [4], wet

deposition [5], road dust [6] and gas phase [7].

Little attention has been paid to the PAHs compounds in Saudi Arabia. The aim of the present study was to evaluate the concentration levels of PAH compounds in the atmosphere of Makkah city, identify the possible sources of PAHs based on diagnostic ratios of PAH compounds, and evaluate health risks associated with inhalation of PAH compounds.

II. PROCEDURE FOR PAPER SUBMISSION

A. Description of Sampling Sites

The Holy City of Makkah (Latitude $19^{\circ} 25' 21''$ North Meridian $46^{\circ} 49' 39''$) is at an elevation of 277 m above the sea level, and ~ 80 km inland from the Red Sea. Transportation facilities related to the Hajj or Umrah are the main sources of emissions during the season of Hajj and the month of Ramadhan. Three measurement locations (Fig. 1) were selected namely: Al-Shebakah, Al-Azizia and Mina, in order to represent different activities and natural factors (Table I).

Fig.1. Map of measurement locations.

TABLE I: CHARACTERISTICS OF MEASUREMENT LOCATIONS.

Site.	Area	Characterization
1	Al-Shebakah,	Residential area is located at the central of Makkah, western area of Haram.
2	Al-Aziziah	Residential area, is located downwind of Haram, has high traffic density, various types of activities.
3	Mina	Residential area, is located in the eastern area of Haram, has high population, and traffic density

B. Sampling

The air samples were collected on glass fiber filters (Whatmann GFA), with 99% collection efficiency [8], using high volume samplers, for 24 hour period, at a height of 3m

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above the ground level. Before sampling, the glass fiber filters were impregnated in acetone to remove all organic compounds, and stored in desiccators until sampling [9].

C. PAHs Analysis and Extraction

The filters were dried, and reweighed to obtain concentrations of particulate matter, TSP, PM₁₀, PM_{2.5}. The filters were stored in dark until analyzed [10]. PAHs were extracted with 10 ml of DCM/n-hexane (1:1), fractionated by column chromatography, and eluted with 20 mL of n-hexane/dichloromethane (1:1, v:v), according to methods previously described [11].

A 2 μ l of the extract was injected on GC-FID, Model HP 6890, equipped with HB5 capillary column (30m x 320 μ m x 0.25 μ m). The GC was calibrated with a diluted standard solution of 16 PAH compounds (Supelco, Inc., Bellefonte, PA), including. Naphthalene (NAP), Acenaphthylene (ACY), Acenaphthene (ACE), Phenanthrene (PHE), Fluoranthene (FLU), Anthracene (ANC), Fluoranthene (FLA), Pyrene (PYR), Benzo(a)anthracene (BaA), Chrysene (CRY), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Dibenzo(a,h)anthracene (DBA), Indeno(1,2,3-c,d)pyrene (IND) and Benzo(ghi)perylene (BgP).

III. RESULTS AND DISCUSSION

The concentrations of PAHs at the sampling sites are shown in Table II, and Fig. 2. The total PAH concentrations ranged between 128.72 to 195.2 ng/m³ with a mean value of 164.67 ng/m³ for TSP, 120.13 to 166.48 ng/m³ with mean value of 137.81 ng/m³ for PM₁₀, and 103.5 to 184.95 ng/m³ with a mean value 132.40 ng/m³ for PM_{2.5}. The lowest PAH was recorded at Al-Azizia (Fig. 2). The total PAH concentrations in Makkah city were between 8 and 18 times higher than those detected in London, 17.23 ng/m³ [12], and Hong Kong 7.42 ng/m³ [13].

PAH compounds were classified according to the number of aromatic rings into: 2-rings, NAP, 1-MNAP and 2-MNAP; 3-rings, ACY, ACE, FLU, ANT and PHE; 4-rings, FLA, PYR, BAA and CHR; and 5-rings, BBF, BKF, BAP and DBA; 6-ring including BGP and IND, (Table II). The 3-ring PAHs were the most predominant compounds, ranged between 27.4 -46.4%, 23.3-31.6% and 28.6-47.8%, for TSP, PM₁₀ and PM_{2.5}, respectively (Fig. 3).

Fig. 2. Total Σ PAHs in different fractions of particulates at measurement locations.

Fig. 3. Percent of Σ PAHs for each ring-type to Σ total-PAHs in different fractions of particulates at measurement locations.

In the present study, the PAHs levels were lower than those found in New Delhi, India [14], and higher than those found in Taichung, Taiwan [15]. The PAHs levels ranged from 6.46 to 31.7 ng/m³ at a residential area, nearby traffic road, and 6.52 to 38.8 ng/m³ nearby commercial and light industrial area, in Hong Kong [16]. All previous studies resulted that vehicular traffic was the major source of PAHs in urban area.

Table III shows the diagnostic ratios of PAHs concentrations. The ratios indicated greater contribution of the traffic sources to the ambient concentrations, in Al-Shebakah. The diagnostic ratios of IND/BGP averaged ~ 5 at the all sampling sites, in all dust fractions, indicating that the main source of PAHs is diesel vehicle. BGP/IND ratios averaged ~ 0.83 , these ratios displayed high percentage of petrol and diesel engines in all sampling sites. However, IND/(IND+BGP) ratios averaged ~ 0.85 for TSP, PM₁₀ and PM_{2.5} in all sampling sites. The obtained ratios were close to the oil combustion ratios, 0.36-0.57, reported in China [17]. The calculated ratios of BAA/(BAA+CRY) ranged between, 0.6 and 1.0, for TSP, PM₁₀ and PM_{2.5} in all sampling sites. These findings are similar to ratios which were measured for diesel engines, 0.38-0.64 [4], and industrial areas, 0.23-0.89 [17].

Typical combustion origin PAHs can be indicated by CPAH species (combustible PAHs species; FLT, PYR, BAA, CRY, BBF, BAP, BGP and IND).

The CPAH/ Σ PAH ratios at sampling sites for each PM fraction are shown in Table IV. The CPAH/ Σ PAH ratios ranged between 0.51 and 0.71, 0.66 and 0.74, and 0.54 and 0.59, for TSP, PM₁₀ and PM_{2.5}. These results agree with those found for non-catalyst equipped automobiles and heavy-duty diesel trucks [78].

BAA, BBF, BAP, DBA and IND are probably considered human carcinogens, whereas ACY, ANC, BgP, FLA, PYR and FLU are not classified as promoters of cancer risk [18]. In the current study, the total carcinogenic compounds, BAA, BBF, BAP, DBA and IND, and Σ PAH for each PM size-fraction at the sampling sites are shown in Fig. 4. The higher concentrations for the total carcinogenic compounds were shown in Al-Shebakah for TSP and PM_{2.5}, in Al-Azizia for PM₁₀, as a consequence of high traffic density.

TABLE II: THE CONCENTRATIONS (NG/M3) OF THE INDIVIDUAL PAH COMPOUNDS AND DIFFERENT CATEGORIES OF PAHS BASED ON AROMATIC RING NUMBER AT MEASUREMENT LOCATIONS.

Compounds/ Site		TSP			PM ₁₀			PM _{2.5}		
		Al-Azizia	Al-Shebakah	Mina	Al-Azizia	Al-Shebakah	Mina	Al-Azizia	Al-Shebakah	Mina
2-ring	NAP	1.463	1.032	0.87	1.683	0.852	0.768	0.8625	2.574	0.8216
	1-MNAP	0.87	0.92	0.858	0.733	0.792	0.757	0.8625	0.96	0.8217
	2-MNAP	0.87	0.92	0.858	0.733	0.792	0.757	0.8625	12.712	0.8217
	Σ2-ring PAHs	3.203	2.872	2.586	3.149	2.436	2.282	2.5875	16.246	2.465
3-ring	ACY	7.345	3.22	12.383	0.935	3.954	7.61	1.1025	3.98	7.9467
	ACE	0.87	0.92	0.858	4.135	0.792	0.757	0.8625	11.964	0.8217
	FLU	11.5	31.746	14.167	9.338	7.474	14.645	0.1	8.95	25.217
	ANT	17.378	13.566	38.483	14.428	12.91	10.122	31.9075	9.716	7.4233
	PHE	22.638	4.036	7.9117	11.648	2.822	6.9683	5.44	18.238	10.573
	Σ3-ring PAHs	59.731	53.488	73.802	40.484	27.952	40.102	39.4125	52.848	51.981
4-ring	FLT ^b	18.523	16.984	10.438	7.808	10.534	9.495	16.5975	21.092	17.53
	PYR ^b	15.728	18.054	21.427	18.483	2.758	7.68	3.9575	8.648	12.983
	BAA ^{a, b}	13.185	55.592	25.503	57.433	51.026	44.97	13.08	43.33	2.615
	CRY ^b	8.65	13.672	18.407	19.403	4.594	16.128	23.4725	0.082	11.32
	Σ4-ring PAHs	56.086	104.302	75.775	103.127	68.912	78.273	57.1075	73.152	44.448
5-ring	BBF ^{a, b}	9.115	33.684	17.34	19.238	20.308	5.668	3.8175	42.078	14.523
	BKF	0.083	0.088	0.08	0.07	0.074	0.0717	0.0825	0.092	0.0783
	BAP ^{a, b}	0.113	0.116	0.11	0.093	0.1	0.097	0.11	0.122	0.1033
	DBA ^a	0.145	0.154	0.143	0.12	0.132	0.125	0.1425	0.158	0.135
	Σ5-ring PAHs	9.456	34.042	17.673	19.521	20.614	5.9617	4.1525	42.45	14.839
6-ring	BGP ^b	0.04	0.04	0.038	0.03	0.03	0.03	0.0375	0.038	0.035
	IND ^{a, b}	0.208	0.214	0.207	0.173	0.19	0.18	0.205	0.22	0.195
	Σ6-ring PAHs	0.248	0.254	0.245	0.203	0.22	0.21	0.2425	0.258	0.23
ΣTotal-PAHs		128.72	195.2	170.08	166.478	120.134	126.83	103.5025	184.95	108.75
Total Carcinogenic		22.77	89.76	43.30	77.06	71.76	51.04	17.36	85.91	17.57
CPAH (combustible)		65.35	138.14	93.26	122.49	89.35	84.07	61.07	115.39	59.11

NAP: Naphthalene, 1-MNAP-2: 1-MethylNaphthalene, 2-MNAP-2: 2-MethylNaphthalene, ACY-3: Acenaphthylene, ACE-3: Acenaphthene, FLU-3: Fluorene, ANT-3: Anthracene, PHE-3: Phenanthrene, FLT-4: Fluoranthene, PYR-4: Pyrene, BAA-4: Benzo(a)anthracene, CRY-4: Chrysene, BBF-5: Benzo(b) fluouanthene, BKF-5: Benzo(k)fluouanthene, BAP-5: Benzo(a)pyrene, DBA-5: Dibenz(a,h)anthracene, BGP-6: Benzo(g,h,i) perylene, IND-6: Indino(1,2,3) pyrene.

^a Carcinogenic compounds. ^b CPAH.

TABLE III: THE RATIOS OF MEAN CONCENTRATIONS OF BAP/BGP, IND/BGP, BGP/IND, IND/(IND+BGP AND BAA/(BAA+CRY AT SAMPLING SITES

Dust Fraction	Site	BAP/BGP	IND/BGP	BGP/IND	IND/(IND+BGP	BAA/(BAA+CRY
TSP	Al-Azi zia	2.83	5.20	0.192	0.84	0.6
	Al-She bakah	2.90	5.35	0.187	0.84	0.8
	Mina	2.89	5.45	0.184	0.84	0.6
PM10	Al-Azi zia	3.10	5.77	0.173	0.85	0.7
	Al-She bakah	3.33	6.33	0.158	0.86	0.9
	Mina	3.23	6.00	0.167	0.86	0.7
PM2.5	Al-Azi zia	2.93	5.47	0.183	0.85	0.4
	Al-She bakah	3.21	5.79	0.173	0.85	1.0
	Mina	2.95	5.57	0.179	0.85	0.2

TABLE IV: CPAH, Σ PAH AND CPAH/ΣPAH RATIOS AT THE SAMPLING SITES

PM/ Site		CPAH	ΣPAHs	CPAH/ΣPAHs
TSP	Al-Azizia	65.35	128.72	0.51
	Al-Shebakah	138.14	195.2	0.71
	Mina	93.26	170.08	0.55
PM ₁₀	Al-Azizia	122.49	166.48	0.74
	Al-Shebakah	89.35	120.134	0.74
	Mina	84.07	126.83	0.66
PM _{2.5}	Al-Azizia	61.07	103.502	0.59
	Al-Shebakah	115.39	184.95	0.62
	Mina	59.11	108.75	0.54

CPAH ,combustible PAHs species

Fig. 4. Total concentrations of PAH and carcinogenic compounds at different sampling sites in Makkah city.

IV. CONCLUSION

The present study confirms the contribution of vehicular traffic, industrial emissions and the incomplete combustion of open waste burning to atmospheric PAHs. The pollution of PAHs in Makkah city should be managed on controlling traffic exhausts. Further work is needed to develop this preliminary investigation, including more measurements in other locations. Typical environment in Saudi Arabia of high temperature and relative humidity, coupled with abundant sunshine, may result in different chemistry of PAHs from that of other geographical regions.

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