Meteorological Influence on Ambient PAH in Abetifi, Ghana

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Abstract – Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous environmental pollutants whose concentration in the environment are subject to various environmental factors. In this study, the effect of meteorology (wind speed, temperature and solar hours) on levels of ambient PAH from a mountainous environment, Abetifi in Ghana was evaluated. Samples were collected every 28-days for a period of two-years by employing passive air sampling (PAS) method with polyurethane foam (PUF) as adsorbent. Mean concentrations of the PAH (Σ_{16} PAHs) recorded in ambient air at Abetifi ranged from below limit of quantification to 8.434 ng/m³ with the most abundant PAH identified to be naphthalene followed by phenantrene and fluoranthene. Positive relationship exists between PAH levels and some meteorological factors. Moderately significant seasonal variations exist. Influence on total Σ_{16} PAH concentration showed wind speed (36%), temperature (32%), humidity (27%) and solar hours (23%). The effect of rainfall pattern revealed an influence of precipitation scavenging. Solar hours showed 11% influence on photo-oxidation.

Keywords: Polycyclic aromatic hydrocarbons, Abetifi, Influence, Rainfall, Solar hours, Wind speed, PUF.

1. Introduction

In recent times global attention has been turned to air pollution. This is most probably because once emitted, the control of the atmospheric pollutants are exceedingly challenging perhaps virtually impossible. Particular interest is the group of polycyclic aromatic hydrocarbons (PAHs) which has inherent toxicity to humans [1, 2] and the environment [3, 4]. PAHs are formed as by-products of combustion, mainly as a result of incomplete combustion or pyrolysis of organic material [5]. PAHs are semi-volatile and are released mostly from anthropogenic activities [3] particularly from wood burning for domestic uses, refuse burning and automobile exhaust [6, 7]. PAHs are well-known to form high levels of DNA adducts, causing mutations, reproductive defects, and cancers in various tissues [8, 9].

In the atmosphere, PAHs are characterized by long range transport and so are found even in remote ecosystems such as the high Arctic as well as far over the Pacific Ocean [10]. Consequently, many Scientists are putting in frantic efforts including using various techniques and methods to provide data on PAH pollution status in the environment [4, 11, 12, 13, 14, 15]. High mountains and mountainous environments are one such environment which have been identified to act as convergence zone for semi-volatile organic pollutants [16, 17, 18] and so must be continually monitored. Having identified the atmosphere as a suitable medium for estimating the spatial distribution and temporal changes in concentrations of such PAHs [16, 19] in such an environment, the level of atmospheric PAHs from one of the highest altitude forest environments in Ghana was assessed with regards the effect of meteorology on the spatial and temporal variations. By this work, data generated will help in achieving the United Nation's millennium and sustainable development goals; environmental sustainability, good health and well-being, sustainable cities and communities and climate action.

2. Experimental Materials and Methods

2.1. Sampling site

Passive air samplers (PAS) were deployed at Abetifi meteorological station, Eastern Region of Ghana (Fig. 1). Abetifi is located on longitude 0.45° W and latitude 6.41° N. A highland (594.7m above sea level) tropical rainforest with a mean annual temperature of 25.2 °C, mean annual precipitation of 1463.85 mm and 84 h of solar hours per year.



Fig. 1: Sampling area, Abetifi in the Eastern Region of Ghana.

2.2 Air sampling

Samples were collected every 28-days for 24 consecutive times. Two PUF-disks samples were mounted in each sapling campaign. PAS-PUF disk with specifications; 0.030 g/cm³, 15 cm diameter and 1.5 cm thickness was used for the sampling. The PUF disks were confined in stainless steel domed chambers, designed to protect the disks from coarse particle deposition, precipitation and sunlight [20]. Prior to the sampler installation, sampling domed chambers were washed and rinsed first with water then with acetone. The PUF disks were also conditioned by first pre-cleaning 8 h in each solvent (acetone and dichloromethane) consecutively using Soxhlet extraction. They were then dried overnight in a heated fume chamber and wrapped in double-layered aluminium foil and placed in zip-lock polyethylene bags and removing excess air. The cleaned PUFs were kept in a freezer prior to deployment. After each sampling duration, exposed PUF disks were wrapped in double-layered pre-cleaned aluminium foil, labelled and placed into zip-lock polyethylene bags. Samples were conveyed to the laboratory in a cool box at 5 °C and stored at -18 °C in the freezer until analysis. PUF disks were installed and removed same day during all sampling campaigns to obtain field blanks.

2.3 Meteorological Parameters

Meteorological information was recorded during the whole period of sample collection using the professional service of the Ghana Meteorological Agency. Wind speed and temperature were monitored continuously at 2 m above the ground using an automatic weather station (Vaisala HydroMet, Finland). Mean values were calculated for the 28-day period during which the PUF disks were deployed (Table 1).

3. Results and discussion

3.1. Concentration of ambient PAH

Concentrations of PAH (Σ_{16} PAHs) recorded in ambient air at Abetifi are summarized in Table 2 with mean concentrations ranging from below limit of quantification to 8.434 ng/m³. In this study gas phase PAHs were generally higher than the particulate ones. This is in conformity to general observation that vapour-phase PAHs are higher than the particulate ones in tropical regions [2, 21, 22]. This observation is also expected as [11] has estimated particulate-phase sampling rate as approximately 10% of the vapour-phase based on the sampling method employed in this work. In the study, ACE and DBahA were found to be below the limit of quantification throughout the study. BghiP and IcdP were also detected just once throughout the study period. The most abundant PAH in the study was identified to be NAPH followed by PHEN and FLT.

Table 1: Sampling period and conditions prevailing at Abetifi, Ghana.								
SC no.	no. ID St Date		Tm Date	Temp.	WD	Hum.	Prec.	S Hrs
1	ABm1	01/01/2010	01/02/2010	26.3	NE	81	41.4	7.8
2	2 ABm2 01/02/2010		01/03/2010	27.3	SW	78	59	8.4
3	ABm3	01/03/2010	06/04/2010	26.7	SW	78	144.1	6.4
4	ABm4	06/04/2010	26/04/2010	26.5	SW	80	115.7	7.5
5	ABm5	26/04/2010	24/05/2010	25.9	SW	81	140.4	7.5
6	ABm6	24/05/2010	21/06/2010	24.7	SW	87	105.8	5.9
7	ABm7	21/06/2010	19/07/2010	23.5	SW	88	108.5	6.4
8	ABm8	19/07/2010	16/08/2010	23.5	SW	93	89	4.8
9	9 ABm9 16/08/2010		13/09/2010	23.7	SW	90	295.1	4.7
10	ABm10	13/09/2010	11/10/2010	24.5	SW	84	359	6.2
11	ABm11	11/10/2010	08/11/2010	25	SW	80	101.7	7.8
12	ABm12	08/11/2010	06/12/2010	25.4	NE	77	67.6	9.1
13	ABm13	06/12/2010	03/01/2011	25.8	NE	59	0	7.3
14	14ABm1403/01/201115ABm1531/01/201116ABm1628/02/201117ABm1728/03/201118ABm1825/04/2011		31/01/2011	26.2	NE	70	106.1	7.8
15			28/02/2011	26.1	SW		79.5	7.9
16			28/03/2011	26.4	SW		109.2	8
17			25/04/2011	25.6	SW		98.5	6.9
18			23/05/2011	24.6	SW		198	6.2
19	ABm19	23/05/2011	20/06/2011	23.3	SW		203.8	5.6
20	ABm20	20/06/2011	18/07/2011	23.2	SW	92	17.9	4.7
21	ABm21	18/07/2011	15/08/2011	24.1	SW	89	198	4.9
22	ABm22	15/08/2011	12/09/2011	24.3	SW	83	286.8	6.2
23	ABm23	12/09/2011	10/10/2011	25.6	SW	78	2.6	9.7
24	ABm24	10/10/2011	07/11/2011	25.8	NE	68	0	8.8

ID=Sample ID, St Date=Start date, Tm Date=Termination date, Temp.=Mean Temperature, WD-Prevailing wind direction, Hum.=Humidity, Prec.= Precipitation, S Hrs=Solar hours.

Table 2: Ambient PAH concentrations found in Abetifi, Ghana.								
РАН	Abbrev Total Minimu		Minimum	Maximum	Mean Monthly			
		Annual Conc.	Conc.	Conc.	Conc. \pm	std.error		
Naphthalene	NAPH	109.637	1.902	20.869	8.434	± 1.648		
Acenaphtylene	ACEN	1.111	0.014	0.142	0.085	±0.013		
Acenaphtene	ACE	BLQ	BLQ	BLQ	BLQ			
Fluorene	FLU	7.06	0.279	0.75	0.543	± 0.038		

Phenantrene	PHEN	45.574	2.06	4.554	3.506	± 0.184
Anthracene	ANT	4.129	0.00	0.524	0.318	± 0.041
Fluoranthene	FLT	31.918	1.289	3.566	2.455	± 0.15
Pyrene	PYR	23.944	0.866	2.475	1.842	±0.113
Benzo(a)anthracene	BaA	3.018	0.099	0.315	0.232	± 0.016
Chrysene	CHRY	4.836	0.193	0.623	0.372	± 0.028
Benzo(b)fluoranthene	BbF	1.444	0.059	0.213	0.111	± 0.011
Benzo(k)fluoranthene	BkF	0.485	0.023	0.063	0.037	± 0.003
Benzo(a)pyrene	BaP	0.329	0.009	0.038	0.025	± 0.002
Indeno(123cd)pyrene	IcdP	0.03	0.00	0.03	_	_
Dibenz(ah)anthracene	DBahA	BLQ	BLQ	BLQ	BLQ	
Benzo(ghi)perylene	BghiP	0.024	0.00	0.024	_	—
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Conc. in ngm⁻³ BLQ – Below limit of quantification

3.2. Effects of meteorological parameters

Table 3 shows the results of correlation analysis between Σ_{16} PAHs and meteorological parameters. The table revealed a moderate positive correlation for solar hours, temperature and wind speed of which wind speed was the highest. A negative association however was observed of rainfall and Σ_{16} PAHs.

3.2.1. Rainfall

A negatively weak correlation observed for Σ_{16} PAHs and rainfall (r = -0.10), an indication that the higher the rainfall, the lower Σ_{16} PAH concentration in the atmosphere at Abetifi. This effect of rainfall on atmospheric PAH concentrations is an implication of precipitation scavenging which is a removal mechanism of atmospheric aerosol [23]. Work done by [24] in Delhi also recorded a negative correlation (r = -0.29) between rainfall pattern and PAH concentration.

	Table 3: Pearson correlation matrix between PAHs and meteorological parameters.								
	wind						BaP	Vap	
	speed	Sun hrs	Rainfall	Temperature	Humidity	BaP	Ratio*	PAH	$\Sigma_{16}PAH$
wind speed	1								
Sun hrs	-0.262	1							
Rainfall	-0.081	-0.531	1						
Temperature	0.117	0.741	-0.386	1					
Humidity	-0.118	-0.138	0.003	-0.143	1				
BaP	-0.212	0.083	0.181	-0.161	0.152	1			
BaP Ratio*	-0.346	0.118	0.152	-0.205	0.233	0.887	1		
Vap PAH	0.357	0.229	-0.106	0.307	0.274	-0.221	-0.170	1	
Σ_{16} PAH	0.388	0.233	-0.103	0.315	0.253	-0.202	-0.185	0.996	1

 $*\overline{B}aP/(BaP+BbF)$

3.2.2. Wind speed

The positive correlation between wind speed and PAH is indicative of the fact that higher wind speeds are associated with higher PAH concentrations in the atmosphere at Abetifi. This influence of wind speed on atmospheric PAH concentrations was evaluated further using the equation, Log[PAH] (ngm⁻³) = m/wind speed (knot⁻¹) + C, where m is gradient and C is the intercept obtained after performing a linear regression [25]. The plot for the measured data (Log[PAH] versus 1/wind speed) (Fig. 2) gave a significant negative gradient (m = -0.09) and revealed that 11% change in the PAH concentration is due changes in the prevailing wind speed which was significant (*p* = 0.006).

Two separate bands of wind speed were observed to prevail during the sampling campaign at Abetifi (Fig. 2). One band was less than 0.35 knot (0.31 - 0.33 knot) and the other, greater than 0.35 knot (0.40 - 0.53 knots). It has been postulated that uptake rate of PUF-disk will significantly depend on wind speed when the wind speed is between >4 and 5 ms⁻¹ (approx. 7.78 - 9.73 knot) [26]. In this work however the prevailing wind speed at Abetifi was far less than 7.78 knot hence the concentration which may be based on uptake rate observed in this work was minimal.



Fig. 2: The log PAH concentration as a function of inverse wind speed.

3.2.3. Temperature

Another meteorological parameter explored in this work with moderate positive correlation was temperature which reveal higher PAH concentrations with increase in temperature. Increasing seasonal trend corresponding with increasing temperature was demonstrated in [10] with a trend wide range of seasonal temperature ranges (2.7 °C -17.9 °C). In this work however, the temperature variation was very close (23.2 to 27.3 °C) and so can be assumed that its influence would be insignificant on spatial variations [3]. Nonetheless the PAH concentrations were further investigated by converting the measured data into the logarithmic form (log vap PAH) and regressed against reciprocal mean temperature (1/T) (°C⁻¹) of each sampling campaign. This was then plotted for the measured data (Fig. 3) and the plot gave a negative gradient (m = -17.1), which revealed that every unit change in temperature was associated with 0.77 ngm⁻³ of change in the PAH concentration (R² = 0.077) but this change was not significant (p > 0.005).



Fig. 3: The log PAH concentration as a function of inverse mean temperature.

3.2.4. Solar hours

The average daily solar hours that prevailed during the sampling campaign in this work was 6.9 hours. The highest solar hours was observed was in November 2011 with 9.7 hours of sunshine followed by what was observed in December 2010 with 9.1 solar hours. In the study, positively moderate correlation (23%) was observed between the PAH concentration and solar hours. Similar to fig. 3, a plot of the logarithmic PAH concentrations (log vap PAH) regressed against reciprocal solar hours (1/sun Hrs) (Hrs⁻¹) for each sampling period was done. The plot gave a negative gradient (m = -1.02) and revealed 8% contributing from solar hours to concentration changes in PAH which was not significant (r= 0.28, p> 0.005).

3.2.5. Photo-oxidation of PAHs

In the presence of sunlight, PAHs undergo photo oxidation [27] by the absorption of the light and this reaction occurs much faster for vapour-phase PAHs than particle-phase ones [2]. Literature data suggest that photoreactions may strongly affect the ratio ANT/(ANT + PHEN) giving rise to ratios close to 0 [28]. ANT and PHEN are vapour-phase PAHs as such they fit for examining the effect of photo-oxidation in the vapour phase [29]. BaP and its isomer BeP are both photosensitive also. Their ratio, BaP/(BaP + BeP) is also used to investigate the effect of photolysis on particle-phase PAHs [30] and are often used as markers of atmospheric particle ageing and photo degradation of PAHs [28]. BeP was not detected in this work so a more atmospherically stable PAH species BbF, [25] was selected i.e. BaP/(BaP + BbF).

The effect of photo-oxidation on the variation of the PAH levels was investigated using the ratio [Ant/(Ant+Phen)] (Fig. 4) and relative benzo[a]pyrene (BaP) ratio [BaP/(BaP + BbF)]. Both ANT and BaP photo-degrade faster than their isomers [31]. The correlation analysis performed between solar hours prevailing at the time of sampling and [Ant/(Ant+Phen)] ratio gave a negative relationship (slope = -18.0, R² = 0.11). This indicates higher solar hours for lower [Ant/(Ant+Phen)] ratios (ratios close to zero) which is suggestive of higher solar hours giving rise to stronger influence of photoreactions (photo-oxidation) on ANT with 11% sunlight influence. The [Ant/(Ant+Phen)] ratio were between 0 and 0.11, an indication of strong photo-degradation of vapour-phase PAHs. This result is in conformity to [32], whose long term study (1991 to 2008), identified [Ant/(Ant+Phen)] as the most seasonal PAH ratio with ratios between 0 – 0.13 for data from London and 0.02 - 0.12 for Glasglow.



Fig. 4: Variations of [Ant/(Ant+Phen)] and solar hours during the sampling periods.

The relative benzo[a]pyrene (BaP) ratio i.e.[BaP/(BaP + BbF)] was also investigated for photo-degradation and particle ageing for PAHs in this study. The correlation between prevailing sun hours and relative BaP ratio showed a

positive relationship (slope = 0.01, $R^2 = 0.01$) contrary to [Ant/(Ant+Phen)] ratio (Figure 4). The influence of sun hours on the particulate PAHs was very minimal (1%).

3.2.5. PAHs source identification

Principal component analysis (PCA) was employed in this study to explore the extent of air pollution and to aid in their source identification. In the PCA, VARIMAX rotation with Kaiser Normalization was used to maximize the sum of the variance of the factor coefficients.

	Factor	Factor	Factor		George 7
	1	2	3	Communality	Choop 2
NAPH	-0.51	0.145	-0.471	0.503	FU
ACEN	-0.214	0.88	-0.214	0.867	1.
ACE	0.569	-0.029	0.382	0.471	*65
FLU	-0.403	0.749	0.277	0.801	1
PHEN	0.744	0.383	0.425	0.881	ent
ANT	0.201	0.901	-0.086	0.859	Iodu
FLT	0.954	-0.073	0.186	0.951	S • Napt
PYR	0.978	0.035	0.127	0.973	ciba
BaA	0.927	0.244	-0.202	0.959	E-0.6 -0.0
CHRY	0.968	-0.154	0.063	0.965	
BbF	0.928	-0.123	0.105	0.886	
BkF	0.895	-0.208	0.303	0.936	
BaP	0.078	-0.044	0.899	0.815	
IcdP	0.9	-0.376	0.145	0.973	E' 5 DCA
BghiP	0.812	-0.307	0.156	0.778	F1g. 5: PCA s
Variance ex	plained b	y each			
factor					
	8.19	2.7	1.73	12.62	
% variance	54.6	18	11.5		

Table 4: VARIMAX rotated factor loading for PAH.



atmospheric PAHs in Abetifi.

Factor loadings > 0.7 are in bold*

Factor scores represent cumulate contribution of the PAH species loaded on a particular factor/principal component. Positive scores in the PCA are discloses of significant load from the presence of such PAH species on air quality. In the analysis, three factors with Eigen values >1 were extracted. The first principal component is plotted against the second principal component (Figure 5).

From the analysis (Table 4), the first principal component in the data set explains more than 54% of total variance and is loaded with medium and high molecular weight PAHs including PHEN, FLT, PYR, BaA, CHRY, BbF, BkF, IcdP, BghiP, these are all identified as vehicular emission markers [33, 34, 35] Factor 1 is therefore vehicular emission source.

PC2 which explains 18% of total variance has high loadings for ACEN, FLU and ANT which are all 3-membered ring PAHs. According to [28], during low temperature pyrogenic processes (such as biomass combustion of straw and firewood) low molecular weight PAHs are usually formed. This group is therefore indicative of biomass combustion. This is expected in that biomass combustion of straw and firewood, municipal wastes was a common practice in the study area.

PC3 accounted for 11.5% of total variance and is exclusively loaded on BaP. Regarding the emissions of BaP as a sole source, other diagnostic ratios are required to confirm that.

4. Conclusion

In this study, I6 PAHs were in quantifiable measures with individual concentrations of up to 8.434 ng/m³. Meteorological factors affecting the levels of atmospheric PAHs in Abetifi were chiefly wind speed and temperature. The

meteorological influence on total Σ_{16} PAH concentration showed wind speed (36%), temperature (32%), humidity (27%) and solar hours (23%). Every unit change in wind speed was associated with 1 ngm⁻³ increase in total PAH level in the air. This study revealed that precipitation scavenging of PAHs occur at Abetifi anytime there is high rainfall and solar hours also showed 11% influence on PAH photo-oxidation. Two main PAH pollution sources were identified from this study; vehicular emission and biomass combustion.

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