Source Apportionment of Atmospheric Polycyclic Aromatic Hydrocarbons (PAHs) in $PM_{2.5}$ at Different Area in Taiwan

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Introduction

Polycyclic aromatic hydrocarbons (PAH) are a group of organic compounds containing only carbon and hydrogen and constituted by two or more aromatic rings fused together. 16 PAHs were listed as priority pollutants by US environmental protection agency (US-EPA). To distinguish by aromatic rings, the more number of PAHs aromatic rings, the more proportion of solid phase increased [1]. PAHs are not only formed by nature, petroleum, but also mainly formed by incomplete combustion processes of organic materials such as biomass combustion, traffic emissions, industrial processes even stationary sources . Its main concern is related to their potential exposure and adverse health effects on humans, that some of them have been identified as carcinogenic and mutagenic. These seven PAH have also been classified by the International Agency for Research on Cancer [2] where BaP was considered as Group 1 (carcinogenic to humans) and Benz[a]anthracene was considered as Group 2A (probably carcinogenic to humans), and other PAH as possibly carcinogenic to humans (Group 2B) [3-7]. The largest sources of environment PAHs were industrial and human activities. E.g. the steam locomotive exhaust, factory activity, home heating equipment and biomass burning [8-10]. This study aims to investigate the seasonal variations of PAHs in Taiwan. Furthermore, to identity the pollution source of ambient PAHs, diagnostic ratio, principal component analysis (PCA) and positive matrix factorization (PMF) models were used.

Materials and methods

To measure the concentration of atmospheric PAHs, one background, one traffic, eight rural, eight urban and six industrial sampling sites were selected in Taiwan during 2013, 2015 and 2017 (Fig.1). The background sampling site was selected on the Yang-Ming Mountain Banbu meteorology station. Urban sampling sites were located in the northern, central, and southern Taiwan and close to the roadside. Rural sampling site was far away from residential and closed to the river. The industrial sampling sites, one was chosen from Taichung Industrial park in, upwind and downwind sides of food processing industry in Taichung and thermal power plant in New Taipei City, and another site was close to Kaohsiung Software Technology Park. The traffic sampling site was chosen from the highway in Taichung which was far away from the urban site without buildings. About ambient air samples of both vapor phase and solid phase of PAHs compounds were collected using high volume sampling trains (Analitica HVS-$PM_{2.5}$) and set the flow rate at 500L/min. The total volume of the air sample was more than 700 m^3 for a typical sampling duration of 1 day. The sampling media were quartz fiber filters and polyurethane foams (PUFs) with XAD-2 adsorbent resin. To identify the possible sources of atmospheric PAHs in Taiwan, diagnostic ratio, principal component analysis (PCA) and positive matrix factorization (PMF) model were used to evaluate the apportionment of PAHs in atmosphere and speculate the relative contribution of various emission sources.

Diagnostic ratios has been widely used to identify the emission sources of PAHs, e.g., pyrogenic and petrogenic sources by ΣLMW/ΣHMW, petrogenic and coal/biomass combustion by Flt/(Flt+Pyr), and traffic emission and coal/biomass combustion by BaP/BghiP. This method is very easy to use, but it cannot give quantitative information on the contribution of PAHs sources, especially for the samples affected by mixed sources. Principal component analysis (PCA) is a multivariate statistical tool to transform the original data set into a smaller one that account for most of the variance of the original data on individual PAHs. By extracting the eigenvalues and eigenvectors from the correlation matrix, principal factors with eigenvalues > 0.6 were chosen. The software Positive Matrix Factorization (PMF, version 5.0), available from U.S. EPA (2014), was used to identify and quantify sources that contribute to ambient PAHs concentrations in Taiwan. Conditional probability functions (CPF) use the time-divided surface winds to determine the sources impact from different wind directions on the local site.

Results and discussion

During the sampling periods, the average concentrations of atmospheric PAHs in solid and vapor phase measured at 20 atmospheric PAHs sampling sites (NU: North Urban; CU: Central Urban; SU: South Urban; CR: Central Rural; I: Industrial; CT: Central Traffic) range from 0.18-2.30 ng/m^3 and 2.62-126.4 ng/m^3, respectively. Significantly higher PAH concentrations were observed in the urban and industrial sites (Fig. 2). And for other 4 industrial sites (I1, I2, I3 and I4), the concentration of downwind sites were higher than upwind sites. In these 20 sampling sites, the vapor phase PAH was higher than solid phase PAH and this has occurred in the previous study. The reason of the high vapor phase PAH was due to the high temperature. The results indicated that the high temperature would lead to a lower solid/vapor PAHs ratio (because of higher vapor phase concentration). In other hand, BaPeq was observed the highest concentration in the industrial and urban sites. There was also had the standard of polycyclic aromatic hydrocarbons in PM$_{10}$ (BaP=1.0 ng/m^3) according to Directive 2004/107/EC. In this study, the BaPeq had not exceeded the standard in each sampling sites. In order to identify the source of atmospheric PAHs, the diagnostic ratio of BaA/(BaA+CHR) was used to classify the emission sources about diesel or gasoline and industrial (Fig. 3). At the 20 atmospheric PAHs sampling sites, the BaA/(BaA+CHR) values of several industrial and urban stations were higher than 0.5, we speculated that the potential sources were classified to industrial activity. On the other hand, diagnostic ratio Ant/(Ant+Phe) were used to classify petroleum and combustion. The pollution source of rural sampling sites was attributed to combustion since these sites were far away from cities and human activities. In urban sites, the pollution source was classified to the diesel or gasoline.

According to the principal component analysis (PCA), rotation factor loafing (RFL) > 0.6 and using the varimax in the factor analysis, the PC1 and PC2 had 40.8%, 31.1% variance in TSP and 42.7%, 16.9% variance in PM$_{2.5}$ (Table 1). Especially high molecular weight PAHs (BaA, Chr, BbF, BkF, BaP, IND, DBA, BghiP) were dominated in PC1 and low molecular weight PAHs (Flu, Flt, Pyr) were dominated in PC2. Factor scores of TSP and PM$_{2.5}$ were displayed the coefficient matrix in Industrial, Urban, Traffic and Rural. Figure 4 showed the group of urban, rural in TSP and PM$_{2.5}$, respectively. To determine the possible emission sources of solid (TSP and PM$_{2.5}$) and vapor phase PAHs, the PMF model used in this study estimated the sources of vapor phase PAHs were 11.6% from stationary sources, 12.7% from petrochemical fuel gas emission and 75.7% from natural environment of volatile organic compounds (Fig. 5). On the other hand, we found the sources of solid phase PAHs were 37.2% in traffic emission (gasoline), 40.7% in traffic emission (diesel) and 22.2% in coal combustion and stationary sources. Traffic emission accounted for 77.9% of pollution source in solid phase PAHs. In addition, natural environment of volatile organic compounds accounted for 75.7% of pollution source in vapor phase PAHs and the reason for the high vapor PAHs was high temperature.Moreover, sources of atmosphere PM$_{2.5}$ were found stationary sources (34.1%), petrochemical fuel gas (19.7%), vehicle emissions (23.5%) and coal combustion (22.7%) in cold season. Factor 1 was dominated to Pyr, Phe, Flu, Flt and Chr. In the previous study, stationary source species (mainly due to the incinerator) arising as Pyr, Phe and Chr. Factor 2 was dominated to Nap, AcPy and Flu. Factor 3 was dominated to BaP, IND and BghiP. Factor 4 was dominated to Flt and Pyr. Furthermore, the sources of atmospheric PAHs in $PM_{2.5}$ were considered as natural environment of volatile organic compounds (29.2%; Nap), stationary sources (17.8%; Acp, Flu, Flt, Pyr), petrochemical fuel gas emission (34.4%; Nap, AcPy, Phe, Flu) and coal combustion (18.6%; Flt, Pyr) in hot season (Fig. 6). The higher atmospheric PAHs concentration (166.2 ng/m^3) measured in hot season may be attributed to the vaporization within the higher temperatures. According to the principal component analysis (PCA), the PC1 had most variance (40.8% and 42.7%) during the sampling period, respectively. In addition, by using PMF model, the sources of vapor and solid phase PAHs had significantly different. The source of vapor-phase PAHs were provided by natural environment of volatile organic compounds (75.7%). The source of solid-phase PAHs in ambient air were provided by traffic emission (diesel) (40.7%). A significant seasonal variation of atmospheric PAHs was observed during the hot and cold season. The contribution of PAHs provided by petrochemical fuel gas emission was raised to 34.4% in hot season.

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Table 1 Source apportionment of atmospheric PAHs in Taiwan by using PCA (Rotation Factor Loafing, RFL >0.6).

	TSP		$PM_{2.5}$	
	PC1	**PC2**	**PC1**	**PC2**
Nap	-0.62	-0.72	-0.52	-0.51
AcPy	0.02	-0.06	-0.21	0.03
AcP	-0.14	0.34	0.69	0.27
Flu	0.11	**0.87**	-0.29	0.37
Phe	0.57	0.48	-0.80	0.04
Ant	-0.11	0.74	0.49	-0.20
Flt	0.53	**0.81**	0.04	**0.89**
Pyr	0.49	**0.81**	-0.31	**0.88**
BaA	**0.86**	0.38	**0.79**	-0.33
Chr	0.46	**0.73**	**0.87**	0.07
BbF	**0.67**	**0.70**	**0.94**	-0.04
BkF	**0.85**	0.01	**0.86**	0.00
BaP	**0.85**	0.31	**0.77**	-0.22
IND	**0.89**	0.37	**0.88**	-0.34
DBA	**0.93**	0.06	0.00	0.20
BghiP	**0.89**	0.31	**0.77**	-0.56

Fig. 1 Locations of stack flue PAHs and atmospheric PAHs sampling sites in Taiwan.

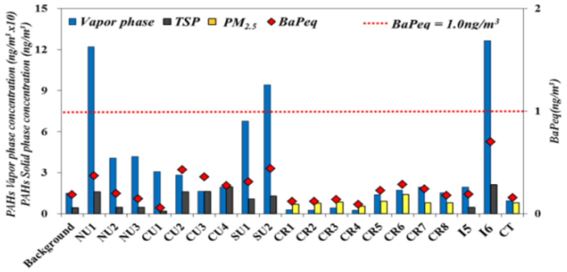

Fig. 2 Atmospheric PAHs solid phase (TSP and $PM_{2.5}$), vapor phase and BaPeq concentration in each sampling sites.

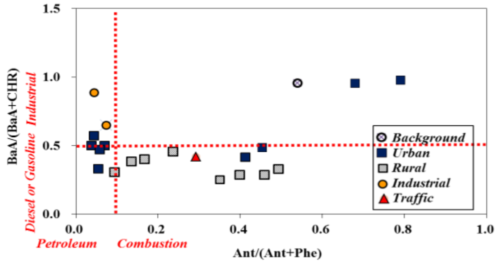

Fig. 3 Source apportionment of atmospheric PAHs at different area in Taiwan by using diagnostic ratio.

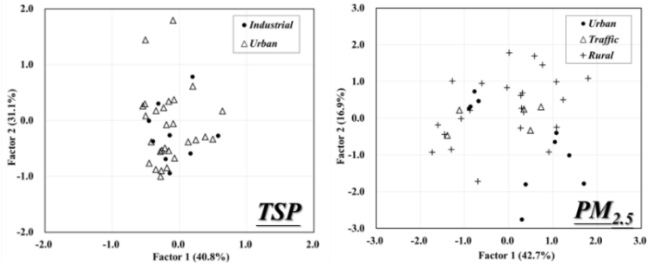

Fig. 4 Factor scores scatter of atmospheric PAHs in Taiwan by using principal component analysis.

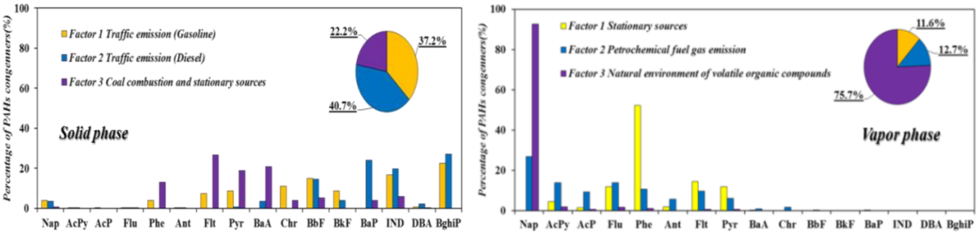

Fig. 5 Source apportionment of atmospheric solid and vapor phase PAHs in Taiwan by using PMF (n=79).

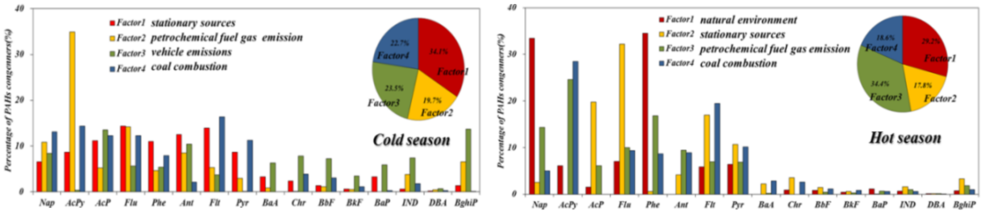

Fig. 6 Source apportionment of atmospheric PAHs during cold and hot seasons in Taiwan by using PMF.