

Polycyclic Aromatic Hydrocarbons Emission in Stack Gases and Source Apportionment in Taiwan Atmosphere

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Introduction

Polycyclic aromatic hydrocarbons (PAH) are organic compounds containing two or more aromatic rings fused together. 24 PAHs were listed as priority pollutants by European Food Safety Authority (EFSA). The more number of PAHs aromatic rings, the more proportion of solid phase increased¹. PAHs mainly originate from incomplete combustion processes of organic materials such as petroleum, natural gases, and biomass. Exposure to PAHs could lead to adverse health effects on humans, some compounds have been classified as carcinogenic or mutagenic. International Agency for Research on Cancer² classified BaP in Group 1 (carcinogenic to humans), Benz[a]anthracene in 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 daily activities, including the steam locomotive exhaust, factory activity, home heating equipment and biomass burning⁸⁻¹⁰, for instance. This study aims to investigate the seasonal variations of PAHs in Taiwan. Furthermore, to identify the pollution source of ambient PAHs using diagnostic ratio, principal component analysis (PCA), and positive matrix factorization (PMF) models.

Materials and methods

The concentrations of atmospheric PAHs were measured at two background, four traffic, eight rural, nine urban and six industrial sampling sites in Taiwan (Fig.1). The background sampling sites were selected on the Yang-Ming Mountain Anbu meteorology station and mount Lulin in the center mountainous area of the island. Urban sampling sites were located in the northern, central, and southern Taiwan and close to the roadside. Rural sampling sites were far away from residential and closed to the river. The industrial sampling sites were selected in the vicinity at industrial park, Software Technology Park, coal-fired power plant, upwind and downwind sides of a food processing industry. The traffic samples were collected from a highway in Taichung which was far away from the urban site without buildings, one was from the tunnel connected Changhua and Nantou, and others were collected at the inlet and outlet of the tunnel in Taipei. Both vapor phase and solid phase of PAHs compounds were collected using high volume sampling trains (Analytica HVS-PM_{2.5}) at the flow rate of 500L/min. The total volume of the air sample was more than 700 m³ 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 $\Sigma\text{LMW}/\Sigma\text{HMW}$, petrogenic and coal/biomass

combustion by Flt/(Flt+Pyr), and traffic emission and coal/biomass combustion by BaP/BghiP. Despite a simple process, this method 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 Positive Matrix Factorization software (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.

Results and discussion

During the sampling periods, the average concentrations of atmospheric PAHs in solid and vapor phase measured at 26 atmospheric PAHs sampling sites (NU: North Urban; CU: Central Urban; SU: South Urban; CR: Central Rural; NI: North Industrial; CI: Central Industrial; SI: South Industrial; NT: North Traffic; CT: Central Traffic) ranged from 0.176~5.97 ng/m³ and 2.62~148 ng/m³, respectively. Highest PAH concentrations were observed in the urban (48.2±41.9 ng/m³) and industrial sites (45.0±52.0 ng/m³) (Fig. 2). And for other 2 traffic sites (NT1 and NT2), the concentration of inlet site was higher than outlet site. In these 26 sampling sites, the vapor phase PAH was higher than solid phase PAH, which was also reported in the previous studies. High temperature might be the reason of the elevation of vapor phase PAHs. Lower solid/vapor PAHs ratio (because of higher vapor phase concentration) was found to correspond to the higher ambient temperature. In other hand, highest value of benzo(a)pyrene (BaP) toxicity equivalent (BaP_{eq}) was observed in the industrial, urban and traffic sites. In this study, the BaP_{eq} of NU3 (1.12 ng/m³) and NU4 (1.09 ng/m³) exceeded the European Union standard (BaP_{eq}=1.0 ng/m³ in PM₁₀, Directive 2004/107/EC). In two stationary emission sources (SS1 and SS2), where pollutants were directly collected from the stacks, concentration of CPM (Condensable particulate matter) (12.2~29.3 mg/Nm³) and FPM_{2.5} (Filterable particulate matter) (0.436~1.91 mg/Nm³) was found. Coal burning boiler (0.07±0.008) had higher FPM_{2.5}/CPM ratio than coal-fired power plant (0.04±0.005). In the other hand, BaP_{eq} concentration of coal burning boiler (7,400±940 ng/Nm³) was higher than coal-fired power plant (5,000±410 ng/Nm³), and PAHs emission factor of coal-fired power plant and coal burning boiler were 317 and 382 µg-PAHs/kg-coal, respectively. According to the principal component analysis (PCA), varimax rotation, the PC1 and PC2 explained 60.6%, 17.9% variance. Congeners including AcPy, Acp, Flu, Ant, FL, Pyr, CHR, BbF, BkF, IND and BghiP dominated the first principle component (PC1), indicated that industrial sampling sites were associated with stack gas, and rural sampling sites were associated with traffic emission. Whereas, BaP was dominant congener in PC2, indicated that PC2 could separate stack gas source and ambient air sampling sites. Stack flue gas was dominated with low rings PAHs and high rings PAHs mostly exist in ambient air (Fig. 3). The diagnostic ratio of BaA/(BaA+CHR) was used to distinguish the emission sources between diesel/gasoline and industry. Diagnostic ratio Ant/(Ant+Phe) was used to classify petroleum and combustion, when the ratio of IND/(IND+BghiP) was used to classify the emission sources of petroleum, liquid fuel combustion, and coal/biomass combustion. The diagnostic ratio of BaP/BghiP was used to separate traffic and non-traffic PAH sources. To sum up, all 26 atmospheric PAHs sampling sites were significantly affected by traffic emission, mainly associated with diesel engine. Stationary sources were mainly influenced by stack gas, fossil fuel volatile/combustion, and coal combustion (Fig. 4). The PMF model estimated the contribution of different sources to atmospheric PAHs in Taiwan. 13.1% of PAHs were from traffic emission (diesel engine) (r=0.82), 17.2% from coal-fired power plant in central Taiwan (r=0.91), 6.30% from cement kiln (r=0.98), 7.38% from coal-fired power plant in northern Taiwan (r=0.70), and 56.0% from coal-fired power plant

in southern Taiwan ($r=0.99$). Moreover, in hot season, sources of atmospheric PAHs were found to be coal-fired power plant in southern Taiwan (59.7%, $r=0.99$), traffic emission (diesel engine) (9.49%, $r=0.77$), natural gas fueled boiler (7.21%, $r=0.56$) and coal-fired power plant in central Taiwan (23.6%, $r=0.93$); whereas in cold season, coal-fired power plant in southern Taiwan (59.0%, $r=0.99$), coal burning boiler (7.33%, $r=0.63$), heavy oil fueled boiler (4.60%, $r=0.96$) and coal-fired power plant in central Taiwan (29.0%, $r=0.89$) (Fig. 5).

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

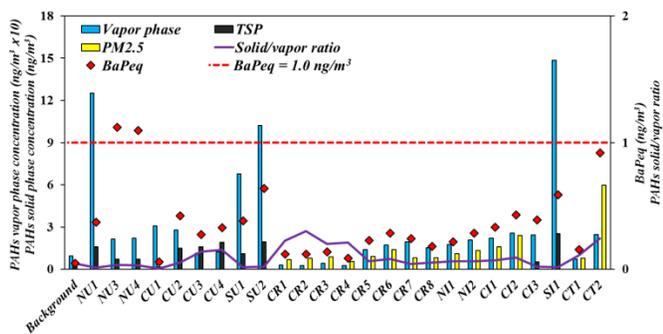


Fig. 2 Atmospheric PAHs solid phase (TSP and PM_{2.5}), vapor phase and BaP_{eq} concentration and solid/vapor ratio in each sampling sites.

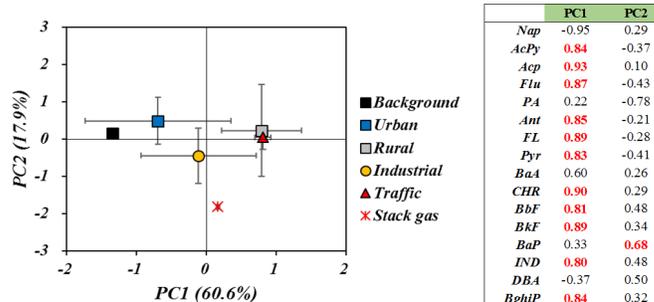


Fig. 3 Source apportionment of atmospheric PAHs in Taiwan by using PCA.

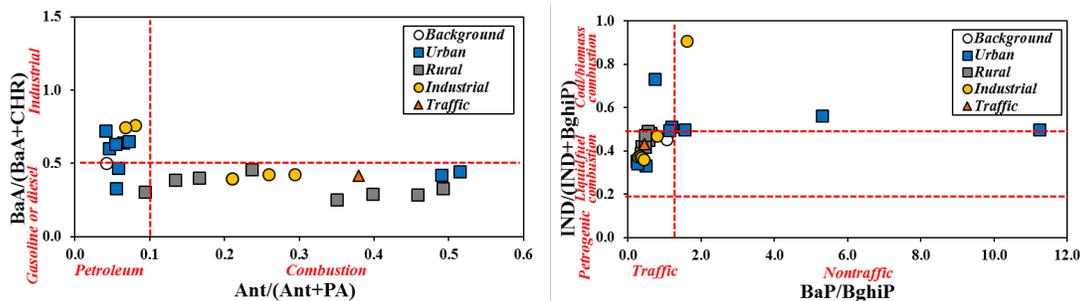


Fig. 4 Source apportionment of atmospheric PAHs at different area in Taiwan by using diagnostic ratio.

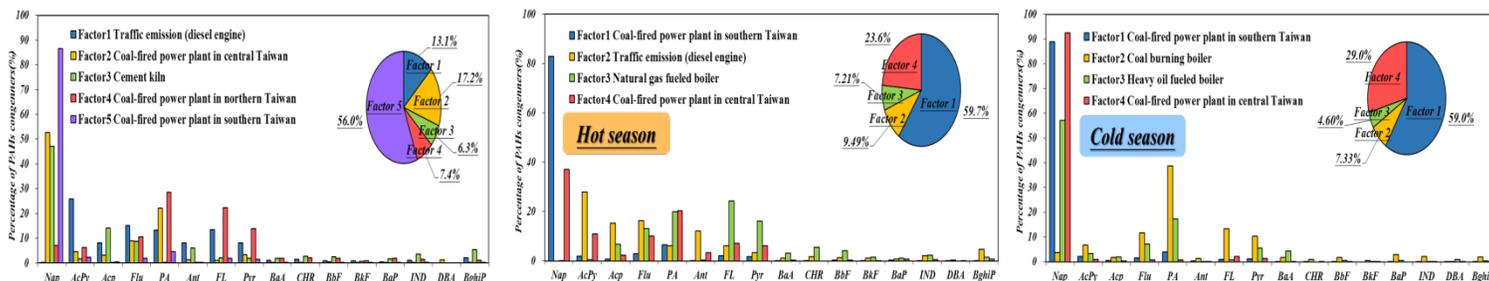


Fig. 5 Source apportionment of atmospheric PAHs in Taiwan by using PMF.