

Source Identification of Atmospheric Polycyclic Aromatic Hydrocarbons (PAHs) in Industrial Complex using Diagnostic Ratios and Principal Component Analysis

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants around the world and some congeners among them are known as carcinogenic chemicals. PAHs are nowadays being described as potential persistent organic pollutants (POPs). Therefore, this study is aimed to identify sources of PAHs in the atmosphere around Sihwa and Banwol industrial areas by using diagnostic ratio of certain PAHs congeners and principal component analysis (PCA). The level of atmospheric PAHs was ranged from 8.07 to 177ng/m³ (gaseous phase: 5.93~68.4ng/m³, particulate phase: 1.85~128ng/m³). From the results of double ratio plots, it is regarded atmospheric PAHs in Sihwa and Banwol industrial complex were originated by combination of traffic emission, coal combustion and petroleum. For higher accuracy of source identification, PCA was carried out for warm and cold period, respectively. As a result, five factors, which accounted for 94.65% and 98.28% of cumulative variance in warm and cold period respectively, were extracted. The main source of atmospheric PAHs was vehicular emission. Coal combustion & incineration-related source was also significant source. Portion of natural gas combustion was increased in cold period and there seemed to be almost no significant influence of petrochemical source even though it accounted for about 10% of total industrial facilities.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds only containing carbon and hydrogen widely distributed in the atmosphere, usually occurring in mixtures. PAHs have been evaluated to be classified as a persistent organic pollutant (POP) due to their persistence, bio-accumulation, potential for long-range environmental transport, adverse effect. Due to these crucial properties, PAHs have been of scientific interest for several decades¹. PAH are formed during almost all forms of combustion, at different ratio depending on the temperature. They can be found naturally in the environment, during such processes as thermal geological reactions and natural fires². But, anthropogenic activities are significant sources to the environment, since PAH are formed in all processes involving incomplete combustion (insufficient oxygen supply) of organic compounds³. Understanding contributions of each source to environment is important and beneficial to appropriate management of PAHs and to further study such as risk assessment⁴. Source identification may be determined using a combination of several techniques such as chemical fingerprinting, diagnostic ratios and multivariate analysis. Usually, there are many studies on source identification using diagnostic ratios of PAHs.

The principal underlying the use of paired PAHs constituents as diagnostic ratio is that PAHs with similar properties (e.g. molecular weight, aqueous solubility and octanol-water partition coefficient) typically retain the same relative concentration in environment as in their sources. This is a convenient and useful tool, however it should be utilized with caution because it is often difficult to differentiate some sources⁵. On the other hand, multivariate analysis can be of great use in the area with numerous pollutant sources^{4,6}. Sihwa and Banwol industrial complex of this study had been prepared from 1986 and 1978 respectively to move scattered industrials of metropolitan area and to derive regional development. There are numerous industrials densely congregated in this area; mainly machinery, petroleum chemistry, steel industry, textile, etc., which account for more than about 60% of the total number. Also, some industrial specified waste incinerators and a cogeneration plant are located. They had caused pollution problems from earlier. Therefore, PAHs concentration in gaseous and particulate atmosphere of these areas was measured for about one year. The objective of this study is to identify PAHs emission sources using various interpretation methods.

Materials and Methods

Atmospheric samples were collected monthly from January 2002 to February 2003. Sampling was carried out on over 4~5 m level from the ground using TSP (total suspended particle) high volume air sampler (HVAS, HV-1000F SHIBATA). HVAS was run for more than 24 hours by each sample with measuring the meteorological condition. Particulate and gaseous PAHs were collected simultaneously. PAHs containing GFFs and PUFs were extracted by accelerated solvent extractor (ASE 2000, DIONEX) using mixed organic solvent (n-hexane and acetone, v:v=1:1). After silica clean-up column, final eluant was used for GC/MS (HP 6890 / HP 5973A) analysis. The deuterated PAHs were used for both calculation of recovery rate and quantification. Surrogate standard materials (d8-naphthalene, d10-acenaphthene, d10-phenanthrene, d12-perylene) were injected prior to extraction and internal standard materials (d10-fluorene, d10-pyrene) were added to clean-up eluant prior to GC/MS analysis. The 16 PAHs, which were designated in U.S. EPA method 610, were measured; Acenaphthylene (AcPy), Acenaphthene (AcP), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Flth), Pyrene (Pyr), Benz[a]anthracene (BaA), Chrysene (Chr), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[a]pyrene (BaP), Indeno[1,2,3-cd]pyrene (IcdP), Dibenzo[a,h]anthracene (DBA), Benzo[ghi]perylene (BghiP).

The basic assumption for receptor models is that the concentration of pollutants at the receptor for a given sample is the linear sum of the products of the emission profile and contribution of sources, and samples are well mixed with chemicals from different sources, and the chemicals are relatively stable during the transport from emission source to the receptor site. PCA is the most widely used tool in environmental science, which reduces the number of variables while retaining the original information as much as possible. In general, each factor extracted from PCA is associated with a source characterized by its most representative chemical(s); PAH compound(s) in this study.

Results and Discussion

The concentration level of total 16 PAHs was ranged from 8.07 to 177ng/m³ (gaseous phase: 5.93~68.4ng/m³, particulate phase: 1.85~128ng/m³). Some studies reported higher level of PAHs was observed in urban and sub-urban area; 11.3 ~ 350 ng/m³ (16 PAHs, gas+particle)⁷, 22.9~410ng/m³ (15 PAHs, particulate phase only)⁸, 668±399ng/m³ (2002) and 672±388ng/m³ (2003) (12 PAHs, particulate phase only)⁹, 235~481ng/m³ (21 PAHs, gas+particle)². Since the relevant sites of above studies were relatively heavily populated, it is regarded high density of traffic and population contributed to the PAHs level. On the other hand, it was reported the PAHs level of industrialized area in Kenya as 128ng/m³ (25 PAHs, particulate phase only)¹⁰. In warm (from March to September) period, the concentration of total PAHs was relatively lower than that in cold period; mean concentration was 18.0ng/m³ (8.07~30.8ng/m³) in warm period and 79.6ng/m³ (26.7~177ng/m³) in cold period. It is mainly because of high temperature leading to increasing photo-decomposition rate of PAHs. In addition, dynamic meteorological condition in warm period which causes dispersion or washing-out effect in the atmosphere, increase of domestic heating and enhanced condensation along with low Henry constant in cold period can cause relatively lower level of PAHs in warm period⁹.

Relative concentration of BaP is commonly used to investigate photo-decomposition of PAHs. BaP is one of the highly reactive PAH congeners with atmospheric condition. In this study, relative BaP concentration is calculated as BaP/(BaP+BbF). In this study, there wasn't a significant variation in BaP/(BaP+BbF) during whole period compared to salient difference in BaP and total PAHs concentration between warm and cold period. It means photo-decomposition is not an important factor for seasonal variation of PAHs concentration.

Among sampling points, a few points are relatively less industrialized; there are rather more residence and traffic in these area. In spite of that, there was almost no significant difference in congener pattern and concentration level compared to other sampling points. This is well supported by multivariate analysis of variance (MANOVA). In the result, there wasn't significant ($p=0.194$, >0.05) difference between sampling points. On the other hand, there was significant ($p=0.000$, <0.05) difference between warm and cold period. As mentioned above, this is due to the characteristics of PAHs to be highly susceptible to temperature.

PAHs diagnostic ratio

Phe, Flth, Pyr (predominant in gaseous phase) and IcdP, BghiP (predominant in particulate phase) account for 68.3% of the total. We can simply expect incineration (or combustion) and vehicle emission as main sources from these indicative congeners. Further consideration can be made for this data set by using various diagnostic ratios of PAHs to identify each source. But, since they are too many, it can make source identification ambiguous and contradictory if calculating all those ratios and considering them simultaneously¹¹. Therefore, diagnostic ratios of a few representative congeners were considered in this study. Figure 1 shows the double ratio plot of them. According to the biplot of BaP/BghiP and Flth/(Flth+Pyr), PAHs of atmospheric samples were mainly contributed by traffic emission and coal combustion in both warm and cold period. On the other hand, in the double ratio plot of IcdP/(IcdP+BghiP) and Flth/(Flth+Pyr), we can see most of samples are located in mixture of

petroleum and combustion. From the results of double ratio plots, it is regarded atmospheric PAHs in Sihwa and Banwol industrial complex were originated by combination of traffic emission, coal combustion and petroleum. It seems to be reasonable to some extent since there are various industrial facilities in this area.

Principal Component Analysis (PCA)

For higher accuracy of source identification, PCA was carried out using SPSS 11.0. In this study, sum of gaseous and particulate phase was used for PCA due to partitioning matter. According to reference 5, the result of PCA can be relatively obvious and it is a little bit easier to identify each factor when using gaseous and particulate data separately. But in the present data set, there wasn't significant difference compared to when using sum of both phase. Axis of each factor can be rotated for easier interpretation of factors extracted by PCA. There are two kinds of rotation methods; orthogonal and oblique. In this study, VARIMAX, which is commonly used orthogonal rotation method, was used. Nap was excluded in input data set due to the uncertainty of its analytical result. Factors with higher eigenvalue than 1.0 were extracted and Table 1 shows the factor loadings of each factor extracted by PCA.

The five factors, which accounts for 94.65% of cumulative variance, were extracted in warm period. Among them, factor 1 (21.73% of the total variance) is predominated by IcdP, DBA and BghiP. This indicates factor 1 is vehicular emission¹². In vehicular emission, it isn't easy to distinguish exhausts of gasoline and diesel. But many studies reported diesel emission showed higher loading of BbF and BkF^{7,11}. So, factor 1 is regarded as gasoline emission. Factor 2 (19.67% of the total) is highly loaded Phe, Flth and Pyr, which are indicative of coal combustion¹³. On the other hand, it has been reported these congeners also indicated incineration^{7,14}. Therefore, factor 2 can be coal combustion or incineration-related source. Factor 3 (18.33 of the total variance) showed high loadings of BbF and BaP with moderate loadings of BaA and BkF, which represents diesel emission^{1,11}. For factor 4 (18.21% of the total variance), the highest factor loadings of BaA and Chr were shown, which is characteristics of natural gas combustion^{1,11}. Factor 5 (16.71% of the total variance) is relative to steel industry source or petro-chemical source. Usually, low molecular PAHs are originated from petro-chemistry. Also it has been reported AcP, AcPy and BaP were indicative of steel & iron industry which used heavy oils as fuel¹⁵.

For cold period, the five factors (98.28% of cumulative variance) were obtained. Factor 1 (29.42% of the total variance) is predominately weighted in IcdP, DBA and BghiP. This profile indicates gasoline vehicular emission¹². Factor 2 (29.09% of the total variance) is highly correlated with Ant, Flth, Pyr, BaA, Chr, BbF, BkF and BaP. Flth, Pyr with BbF and BkF are indicative of diesel emission¹⁴. In addition, BaA and Chr are most highly loaded in factor 2. According to reference 1, BaA and Chr means mixture of diesel and natural gas combustion. This is also supported by reference 13, which reported natural gas combustion had characteristics of high BaA and Chr with moderate Flth and Pyr. Thus factor 2 is considered as mixture of diesel emission and natural gas combustion. Factor 3 (16.22% of the total variance) shows pattern of coal combustion or incineration-related source (high loading of Flu, Phe, Flth and Pyr) like factor 2 of warm period^{7,14}. For factor 4 (11.96% of the total variance), AcPy and Flu are highly loaded. And AcP, Flth, Pyr (low molecular PAHs) and

BaA seem to be somewhat correlated with factor 4. This indicates factor 4 can be regarded as petrochemical source or steel industry source which is using heavy oils as fuel¹⁵. In case of factor 5 (11.59% of the total variance), AcP (0.92) showed the highest loading with Chr (0.55). When we consider AcPy and BbF together, factor 5 is likely to be stationary emission. But, there seems to be lack of additional information for identification of factor 5.

With speaking about main sources, it can be assumed that similar results with double ratio plots were obtained from PCA even though PCA showed slightly different aspect by period (warm or cold). Vehicle emission seems to be main source of atmospheric PAHs. Coal combustion & incineration-related source was also significant source. In Sihwa and Banwol industrial complex, there are about a few hundreds of medium/small sized incinerators scattered and steel industry facilities which is one of main types of industry in this area. It was shown natural gas combustion was increased in cold period. And there seemed to be almost no significant influence of petro-chemical source even though it accounted for about 10% of total industrial facilities.

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Figure 1. Double ratio plot of BaP/BghiP and Flth/(Flth+Pyr), IcdP/(IcdP+BghiP) and Flth/(Flth+Pyr).

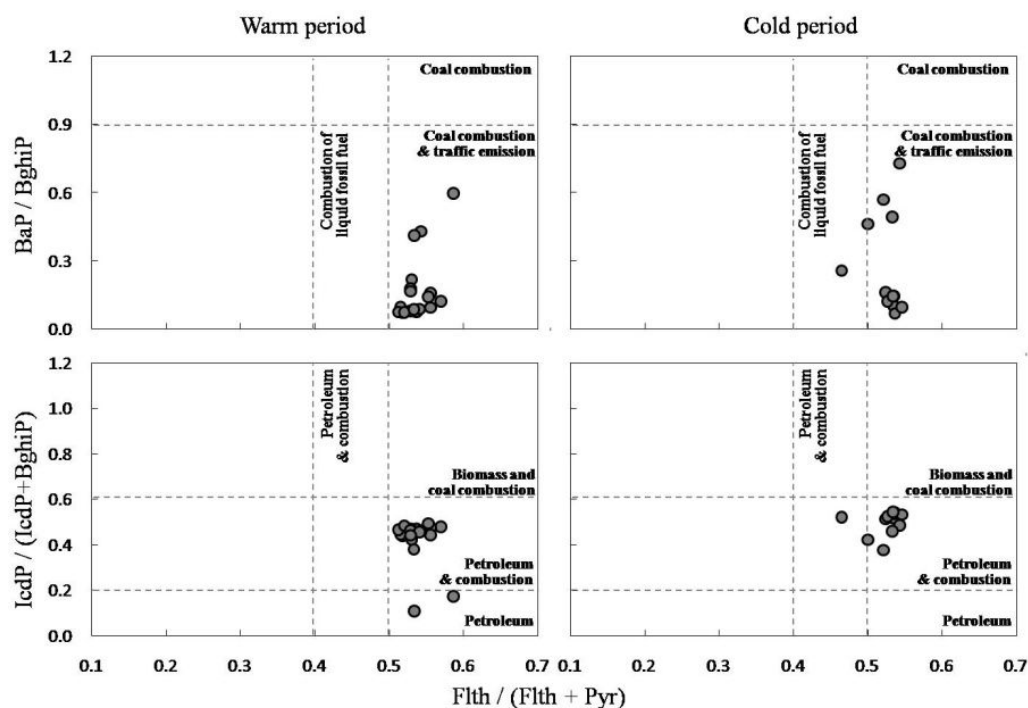


Table 1. VARIMAX-rotated factor loadings of PCA for both warm and cold period.

Congeners	Warm period ^{a)}					Cold period ^{a)}				
	fac-1	fac-2	fac-3	fac-4	fac-5	fac-1	fac-2	fac-3	fac-4	fac-5
AcPy	0.14	0.30	-0.13	0.03	0.91	-0.11	0.30	0.10	0.86	0.38
AcP	0.06	-0.06	-0.08	0.06	0.97	-0.14	0.16	0.05	0.31	0.92
Flu	0.67	0.07	-0.06	0.48	0.45	0.02	0.46	0.56	0.63	0.21
Phe	0.33	0.69	0.12	0.22	0.55	0.08	0.27	0.95	0.07	0.04
Ant	0.45	0.48	0.29	0.58	0.22	0.50	0.83	0.15	0.15	0.03
Flth	0.30	0.82	0.39	0.21	0.12	0.44	0.61	0.52	0.30	0.17
Pyr	0.37	0.82	0.32	0.24	0.10	0.40	0.60	0.56	0.33	0.15
BaA	0.04	0.14	0.42	0.86	-0.12	0.14	0.78	0.33	0.41	0.28
Chr	0.26	0.15	0.02	0.91	0.18	-0.30	0.61	0.42	0.20	0.55
BbF	0.12	0.31	0.88	0.16	-0.10	0.53	0.61	0.35	0.14	0.42
BkF	0.53	0.38	0.46	0.55	0.13	0.45	0.75	0.32	0.22	0.26
BaP	0.21	0.17	0.92	0.23	-0.10	0.60	0.70	0.27	0.21	0.04
IcdP	0.88	0.35	0.19	0.16	0.16	0.97	0.17	0.08	-0.08	-0.10
DBA	0.55	0.50	0.52	-0.01	-0.16	0.97	0.21	0.01	-0.01	-0.06
BghiP	0.87	0.34	0.25	0.22	0.09	0.96	0.22	0.10	-0.02	-0.08
eigenvalue ^{b)}	3.26	2.95	2.75	2.73	2.51	4.41	4.36	2.43	1.79	1.74
% variance	21.73	19.67	18.33	18.21	16.71	29.42	29.09	16.22	11.96	11.59

^{a)} Factor loadings higher than criteria were highlighted; 0.4 in warm period and 0.5 in cold period.

^{b)} Factors with higher eigenvalue than 1.0 were extracted.