

The use of polycyclic aromatic hydrocarbons molecular diagnostic ratios as a source identification tool – case study

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Abstract. Levoglucosan (LG) and Polycyclic Aromatic Hydrocarbons (PAHs) are organic substances emitted from variety of anthropogenic sources, mainly as a result of incomplete combustion or pyrolysis of organic material. The seasonality of PAHs emissions is a well demonstrated fact, observed in most monitoring studies, where PAHs air concentrations in winter are much higher than their respective in the summer, due to seasonally variable emission sources. Various techniques have been proposed as ideal source identification (or apportionment) tools, and much debate exists in scientific literature about the effectiveness of the proposed methodologies. The most common methodology is the use of molecular diagnostic ratios (MDRs). Based on the annual measurement campaign in rural site located on South Poland, were levoglucose and PAHs were analyzed, the MDRs were determined. The results showed that the combustion processes of solid fuels, including biomass, are mainly responsible for air quality.

1 Introduction

Polycyclic aromatic hydrocarbons are a large group of organic compounds which have cyclic structure and similar physicochemical properties. Although more than 100 different PAHs are known, in environmental samples 16 of them are most commonly determined - due to their toxicological properties. PAHs belong to the group of the most commonly occurring, stable organic pollutants. PAHs are emitted from natural sources, e.g.: volcanic eruptions, as well as anthropogenic sources, such as thermal transformation of solid and gaseous fuels, waste etc. [1-4]. The concentration of PAHs in the air depends on: the distance from the source of emission, the height of the emission source, meteorological conditions and the season of the year.

Various techniques have been proposed as ideal source identification (or apportionment) tools, and much debate exists in scientific literature about the effectiveness of the proposed methodologies. The most common methodology is the use of molecular diagnostic ratios (MDRs) [5,6]. The main ratios used in order to give insight about the responsible sources are given in Table 1.

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The aim of the publication is to identify potential sources of PAHs emissions in rural areas, using the example of measurement campaign in health resort.

Table 1. Most commonly used PAH MDRs [7-9] ANT: anthracene; PHE: phenanthrene; BaA; benzo[*a*]anthracene; CHR: chrysene; FLT: fluoranthene; PYR: pyrene; IPY: indeno[1,2,3-*c,d*]pyrene; BPE: benzo[*g,h,i*]perylene.

Correlation	Petrogenic	Pyrogenic
ANT/(ANT + PHE)	<0.1	>0.1
BaA/(BaA + CHR)	<0.2	>0.35
FLT/(FLT + PYR)	<0.4	>0.4
IPY/(IPY + BPE)	<0.2	>0.2
	Fuel combustion	Grass/coal/wood combustion
FLT/(FLT + PYR)	0.4–0.5	>0.5
IPY/(IPY + BPE)	0.2–0.5	>0.5

2 Methods

2.1 Sampling point

Aerosol samples were collected in the „A” zone of health resort, on climatological station IMGW-PIB department in Cracow ($\varphi=49^{\circ}24'28''$ $\lambda=20^{\circ}57'39''$, $h= 582$ m ASL.). The health resort area is agricultural and forest land with high tourist attractions. Due to land development, the station can be qualified as a representative for the rural background. Sampling campaign was carried out from March 2016 to April 2017. Dust samples were collected with the use of low flow sampler with separating head PM₁₀ Atmoservice PNS3D15/ LVS3d, with stabilized flow 2.3 m³/h. Dust samples collection and gravimetric analysis were done according to PN-EN 12341:2014 Ambient air. Standard gravimetric measurement method for the determination of the PM₁₀ or PM_{2.5} mass concentration of suspended particulate matter. Samples were collected at 24-hour cycle on 47 mm Whatman QMA quartz filters.

2.2 Analytical methods

Concentration of PAHs was determined by GC/MS methods. The samples were collected to the month average sample and placed in a reaction vial. Internal standard, deuterated mixture of 7 PAHs, were added. Samples were extracted in ultrasonic field with 3 portions of dichloromethane. Then, the extracts were concentrated and analyzed by using GC-2010 Shimadzu gas chromatograph (Shimadzu, USA) coupled with mass spectrometry detector equipped with a 30m, 0.25-mm i.d. HP-5MS capillary column. Calibration was performed in the range from 0.015 to 3.0 µg/mL. Precision expressed as a relative standard deviation were calculated to be from 1.3 to 12.8%.

3 Results

The seasonality of PAHs emissions is a well demonstrated fact, observed in most monitoring studies, where PAHs air concentrations in winter are much higher than in the summer, due to seasonally variable emission sources like space heating or cold engine start of vehicles etc. During the measurement campaign, the total PAHs concentration varied from 3.4 ng/m³ (June 2016) to 275 ng/m³ (January 2017). The results of the study showed a significant variation in the concentration of PAHs depending on the season. In the heating season, the total PAHs concentration was on average 100.8 ng/m³, while in the non-heating season only 5.9 ng/m³. Such a significant difference in the total PAH concentration in the air indicates a significant impact of local emission sources on air quality. Detailed profile of PAHs is presented in Table 1.

The benzo[*a*]pyrene-equivalent (BaPE) index (ng/m³) is one of the parameters describing the carcinogenic potential of PAHs in atmospheric dust [10]. The BaPE values determined on the PAHs concentrations according to Formula 1 were ranged from 0.79 in July 2016 to 22.4 in January 2017.

$$BaPE = 0.06 \cdot BaA + 0.07 \cdot (BbF + BkF) + BaP + 0.6 \cdot DahA + 0.08 \cdot IP \quad (1)$$

Where: BaA – benzo[*a*]anthracene, BbF – benzo[*b*]fluoranthene, BkF – benzo[*k*]fluoranthene, BaP – benzo[*a*]pyrene, DahA – dibenzo[*a,h*]anthracene, IPY – indeno[1,2,3-*c,d*]pyrene

The obtained results indicated a much higher carcinogenic potential of dust in the heating period, compared to non-heating. The BaPE changes during the annual measurement campaign is shown in Figure 1.

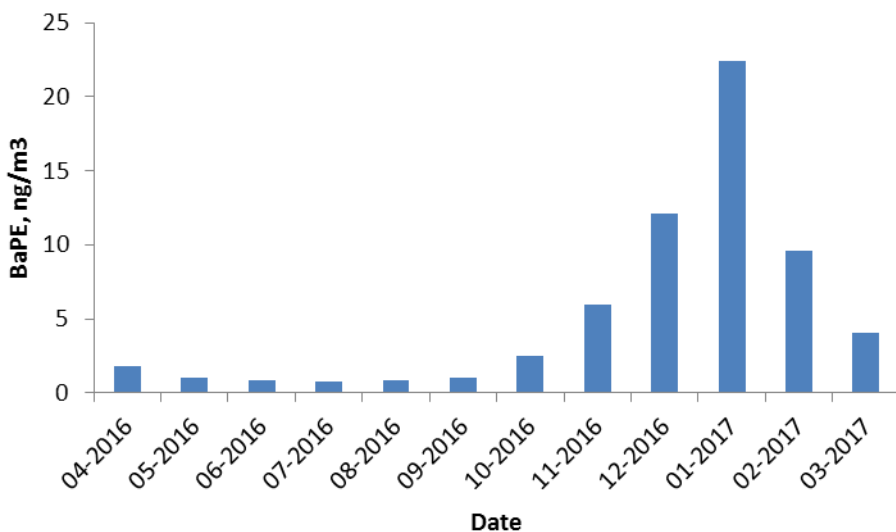


Fig. 1. The BaPE changes during the annual measurement campaign

Common methodology used to identify emission sources of this type of compounds based on molecular diagnostic ratios (MDRs), as the basic indicators assumes the dependencies: anthracene vs phenanthrene (ANT/(ANT+PHE)); benzo[*a*]anthracene vs chrysene (BaA/(BaA+CHR)); fluoranthene vs pyrene (FLT/(FLT+PYR)); indeno[1,2,3-*c,d*]pyrene vs benzo[*g,h,i*]perylene (IPY/(IPY+BPE)); benzo[*a*]pyrene vs

benzo[*g,h,i*]perylene (BaP/(BaP+BPE)). It is known that the ratio ANT/(ANT+PHE) has been suggested as an indicator of petrogenic against pyrogenic sources. This ratio has been criticized in the past [5,6]. Because of the fact anthracene is more reactive than phenanthrene, and therefore their environmental fate is much different. The ratio ANT/(ANT+PHE) is therefore anticipated to change significantly from a given source. Due to the fact that the campaign was carried out in the area of the health resort, there are no large PAHs emitters in the immediate vicinity, the dependence has not been determined. The BaA/(BaA+CHR) ratio is supposedly able to discriminate between the same sources as ANT/(ANT+PHE). A value below 0.20 suggests petrogenic emissions, while a value > 0.35 cation combustion (pyrogenic emissions). During the measurement campaign, the BaA/(BaA+CHR) ratio ranged from 0.28 in August 2016 up to 0.56 in January 2017 (Table 2). The obtained results indicate a significant impact of combustion emissions on air quality. Monthly change of BaA/(BaA+CHR) during the campaign is shown in Figure 2.

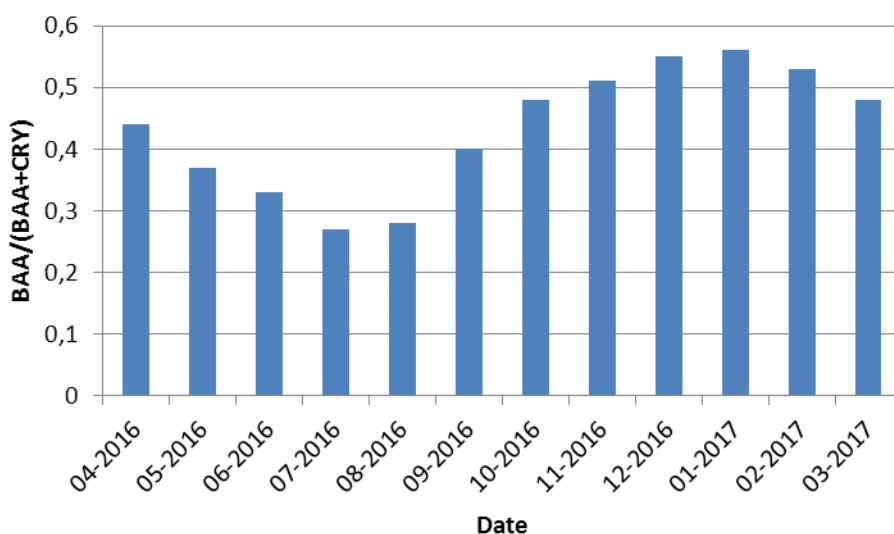


Fig. 2. Monthly change of BaA/(BaA+CHR) during the campaign

FLT/(FLT+PYR) can also according to the MDRs methodology differentiate between petro- and pyrogenic sources (<0.40 and >0.40, respectively), but can also give insight on whether the pyrogenic emissions are due to fuel combustion (0.4-0.5), or due to combustion of other materials (>0.50). In the presented studies, the ratio was above 0.50 in the entire measurement campaign. The lowest value - 0.51 was in October 2016, the highest - 0.59 was observed in July and August 2017 (Table 2). The value of this ratio indicates that the PAHs emission is mainly the result of biomass burning, independent of the season.

Table 2. Concentration of PAHs during April 2016 – March 2017

Compound	04-2016	05-2016	06-2016	07-2016	08-2016	09-2016	10-2016	11-2016	12-2016	01-2017	02-2017	03-2017	Average annual
Naphthalene	0.063	0.033	0.065	0.053	0.067	0.049	0.054	0.066	0.208	0.272	0.341	0.245	0.126
Acenaphthylene	0.038	0.006	0.001	0.000	0.000	0.008	0.044	0.100	0.353	0.827	0.315	0.119	0.151
Acenaphthene	0.020	0.014	0.016	0.010	0.015	0.003	0.009	0.013	0.023	0.050	0.020	0.018	0.017
Fluorene	0.033	0.013	0.005	0.009	0.013	0.007	0.035	0.048	0.112	0.306	0.155	0.075	0.068
Phenanthrene	0.625	0.192	0.102	0.155	0.217	0.132	0.518	1.113	3.464	14.492	4.361	1.627	2.250
Anthracene	0.071	0.016	0.000	0.002	0.004	0.006	0.075	0.229	1.140	4.146	1.057	0.220	0.581
Fluoranthene	1.335	0.465	0.148	0.140	0.248	0.300	1.493	5.302	18.904	56.054	17.882	5.297	8.964
Pyrene	1.211	0.390	0.106	0.096	0.175	0.283	1.457	5.034	16.611	45.693	14.650	4.476	7.515
Benzo[<i>a</i>]anthracene	0.940	0.248	0.059	0.056	0.083	0.207	1.806	7.209	19.912	40.218	15.039	3.877	7.471
Chrysene	1.210	0.418	0.122	0.150	0.211	0.314	1.930	6.798	16.585	31.440	13.252	4.175	6.384
Benzo[<i>b</i>]fluoranthene	1.410	0.622	0.156	0.182	0.280	0.505	1.897	5.093	11.294	20.257	9.346	4.020	4.589
Benzo[<i>k</i>]fluoranthene	1.182	0.511	0.120	0.125	0.200	0.424	1.749	4.798	8.777	16.378	7.318	3.540	3.760
Benzo[<i>a</i>]pyrene	1.358	0.844	0.689	0.663	0.695	0.837	1.916	4.450	8.767	16.146	6.906	2.990	3.855
Indeno[1,2,3- <i>c,d</i>]pyrene	1.442	0.976	0.771	0.743	0.783	0.982	1.923	3.950	7.512	13.356	6.179	2.722	3.445
Dibenzo[<i>a,h</i>]anthracene	0.841	0.773	0.758	0.732	0.741	0.776	0.970	1.223	1.755	3.008	1.561	0.982	1.177
Benzo[<i>g,h,i</i>]perylene	1.020	0.558	0.302	0.287	0.349	0.538	1.480	3.732	7.000	12.443	5.669	2.683	3.005
Total	12.800	6.078	3.419	3.405	4.082	5.370	17.356	49.158	122.417	275.084	104.052	37.066	

Table 3. Index BaPE and PAH diagnostic ratios

Parameter	04-2016	05-2016	06-2016	07-2016	08-2016	09-2016	10-2016	11-2016	12-2016	01-2017	02-2017	03-2017	Average
BaPE	1.76	1.06	0.82	0.79	0.84	1.04	2.49	5.96	12.07	22.37	9.56	4.03	-
IPY/(IPY+BPE)	0.59	0.64	0.72	0.72	0.69	0.65	0.57	0.51	0.52	0.52	0.52	0.50	0.59
BaA/(BaA+CRY)	0.44	0.37	0.33	0.27	0.28	0.40	0.48	0.51	0.55	0.56	0.53	0.48	0.43
FLT/(FLT+PYR)	0.52	0.54	0.58	0.59	0.59	0.51	0.51	0.51	0.53	0.55	0.55	0.54	0.54

The IPY/(IPY+BPE) ratio is said to offer similar interpretations to FLT/(FLT+PYR). The determined IPY/(IPY+BPE) ratio reached values from 0.48 in March 2017 to 0.72 in June and July 2016 (Table 2). Trend IPY/(IPY+BPE) vs month is presented in Figure 3. According to Yuner et al. [7] IPY/(IPY+BPE) above 0.50 is the result of grass and wood combustion. The obtained dependences, especially the IPY/(IPY+BPE) value in the summer months, indicates a significant effect of biomass combustion on air quality.

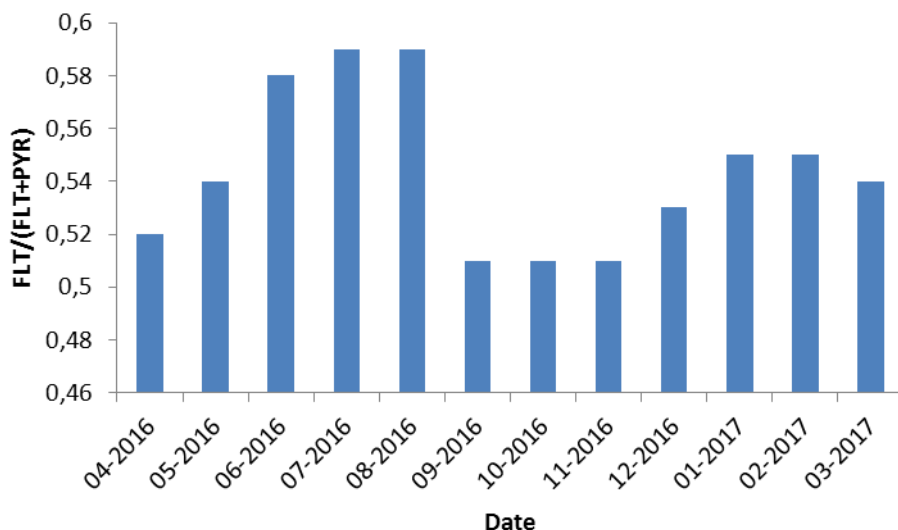


Fig. 3. Monthly change of IPY/(IPY+BPE) during the campaign

4 Conclusions

The measurement campaign results showed:

- a greater carcinogenic potential of dust in the heating period, compared to non-heating;
- a significant impact of emissions from fuel combustion processes on the air quality.

Analysis of data from the annual measurement campaign using the MDRs method, based on the value of IPY/(IPY+BPE) and FLT/(FLT+PYR) ratios, suggests a significant impact of fuel combustion including biomass on air quality in this area.

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