

VARIABILITY OF GAS-PARTICLE PARTITIONING OF POLYCYCLIC AROMATIC HYDROCARBONS IN A PILOT AREA OF VOJVODINA

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Abstract:

Polycyclic aromatic hydrocarbons consist of two to eight condensed aromatic rings and they are produced during incomplete combustion of organic materials. High atmospheric levels of polycyclic aromatic hydrocarbons are associated with industrial activities, energy production, and any type of combustion and traffic. In the atmosphere, PAHs are distributed between gaseous and particulate phase. Distribution of PAHs in the atmosphere controls removal processes and atmospheric degradation. During the June and July 2004 air sampling campaign was conducted in the region of Vojvodina, and concentration levels of 16 PAHs in gaseous and particulate phases were determined.

Keywords:

Polycyclic aromatic hydrocarbons; Gas-particle partitioning; Atmospheric distribution; Active air sampling

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are the complex group of organic compounds with planar structure, with C and H atoms organized in circlet structure with at least two aromatic rings. Primary natural sources of PAHs are fires and volcanic eruptions. The most important anthropogenic sources of PAHs in the atmosphere are wood combustion, energy production, and production of aluminium, incineration, catalytic cracking and exhaust gases from vehicles. Concentration levels and behavior of polycyclic aromatic hydrocarbons in the environment have been frequently monitored because of their long-term transport, global distribution and high toxicity [1, 2, 3, 4, 5].

In the atmospheric environment, PAHs are found in the gaseous phase or sorbed at the solid particles, depending mainly on ambient temperature and vapor pressures. Gas-particle partitioning process can be described using partitioning coefficient K_p :

$$K_p = \frac{F}{K_v} = \frac{TSP}{A} \quad (1)$$

where:

K_p – partition coefficient between particle and gaseous phase in atmosphere ($\text{m}^3 \mu\text{g}^{-1}$)

K_v – partition coefficient between gaseous and particle phase in atmosphere ($\mu\text{g m}^{-3}$)

A i F – compound concentration associated with the gaseous and particle phase, respectively (ng m^{-3} air)

TSP – total suspended particulate matter concentration ($\mu\text{g aerosol m}^{-3}$ air)

Atmospheric distribution of PAHs, can also be described with total amount of substance proportion sorbed on atmospheric particles, ϕ :

$$\phi = \frac{F}{A + F} = \frac{K_p \cdot TSP}{1 + K_p \cdot TSP} \quad (2)$$

During the period from June - July 2004, air sampling campaign was conducted in the region of Vojvodina, Serbia, and concentration levels of 16 US EPA PAHs were determined.

2. MATERIALS AND METHODS

Concentration levels of selected polycyclic aromatic hydrocarbons have been determined in accordance with the sampling procedure and analysis of organic pollutants in ambient air, adopted by EPA [6, 7]. Active air sampling method is realized through flowing of definite quantity of air,

controlled by compressor, through the sampler. In the first step, air is released through the horizontally placed single layer filter made of glass fiber (GF), which holds atmospheric particles over 0.1 μm in diameter. Air, then, passes through the sorbent made of polyurethane foam (PUF), placed behind GF, which collects gaseous phase of PAHs molecules.

The sampler used for the active sampling of air was GV2360 Thermo Andersen TSP, made of stainless steel boxes and equipped with 20.32 x 25.4 cm filter holder and PUF holder (9 cm in diameter and 30 cm long). Air was passed through using a 1200 watt motor controlled by an inverter (Hitachi L100-015NPE) and flow was measured by a Sierra 620 fast flow insertion mass flow meter with a totaliser. The average total sampled air was 1200 m^3/day . For each sampling period, per one Whatman grade G653 glass fiber filter (dimension: 20.32 x 25.4cm) and two polyurethane foam filters (dimension: 9 cm diameter and 5 cm long) were used.

Prior the sampling, glass fiber filters were burned in 400°C for 5 hours and polyurethane foam filters were Soxhlet extracted by 1:1 acetone/hexane (Merk suprasolv) by a Foss Tecator Soxtec 1045 HT-2 apparatus for 4 hours to 120°C.

After the sampling period (3 x 24h), GFs and PUFs were extracted and analyzed using GC/MS method. Analytical determination of 16 EPA PAHs in all samples was carried out in laboratories of Research Centre for Environmental Chemistry and Ecotoxicology (RECETOX), Masaryk University in Brno, Czech Republic.

3. RESULTS

Three 24-hour high volume samples were collected from each of three sampling sites in in the town of Pančevo, Vojvodina, Serbia. Air sampling campaign in Pančevo was conducted during the period from 27th – 30th June, 2004. Two samplers were placed within the industrial area, in the yard of the oil refinery and petrochemical complex (localities P1 and P2, respectively). The third HiVol sampler was placed in the city center, on the top of the Pančevo city hall (locality P3). Detailed information on the three sampling spots is presented in Table 1. Concentration levels of 16 EPA PAHs are presented in Table 2.

Table 1. Detailed information on the sampling sites

Site ID	Latitude	Longitude	Elevation (m a.s.l.)
P1	N 44°49' 56.3"	E 20°41' 25.4"	82
P2	N 44°49' 57.0"	E 20°40' 17.0"	85
P3	N 44°52' 12.8"	E 20°38' 24.1"	130

Table 2. Average concentrations of PAHs in gaseous and particulate phase (ng/m^3)

Sample type	PUF	GF	PUF	GF	PUF	GF
Locality	P1		P2		P3	
Sampling period	27-30th June 2004					
Nap	1.195	0.010	0.811	0.016	0.454	0.010
Acy	0.065	0.003	0.050	0.001	0.044	0.001
Ace	0.063	0.006	0.054	0.006	0.027	0.002
Flo	1.454	0.003	1.497	0.009	0.171	0.002
Phe	18.309	0.041	27.364	0.144	3.659	0.030
Ant	0.679	0.001	1.152	0.007	0.187	0.002
Flu	2.133	0.024	10.997	0.167	2.160	0.071
Pyr	1.521	0.020	3.773	0.095	1.831	0.077
B(a)A	0.023	0.008	0.017	0.018	0.070	0.028
Chr	0.120	0.018	0.146	0.066	0.206	0.088
B(b)F	0.041	0.045	0.019	0.220	0.029	0.380
B(k)F	0.022	0.030	0.010	0.122	0.012	0.144
B(a)P	0.021	0.016	0.006	0.102	0.000	0.130
I(1,2,3-cd)P	0.021	0.046	0.005	0.240	0.000	0.365
D(ah)A	0.000	0.002	0.000	0.013	0.000	0.024
B(ghi)P	0.035	0.066	0.009	0.320	0.000	0.500
Total	5.700	0.336	45.909	1.547	8.849	1.853

Estimated distribution of polycyclic aromatic hydrocarbons between gaseous and particulate phase in the ambient air of Pancevo is shown in Figures 1 – 3.

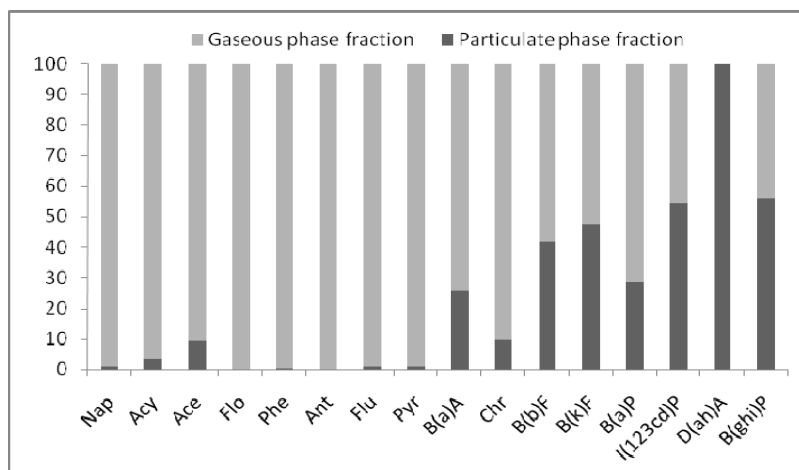


Figure 1. PAH distribution between gaseous and particulate phase at locality P1

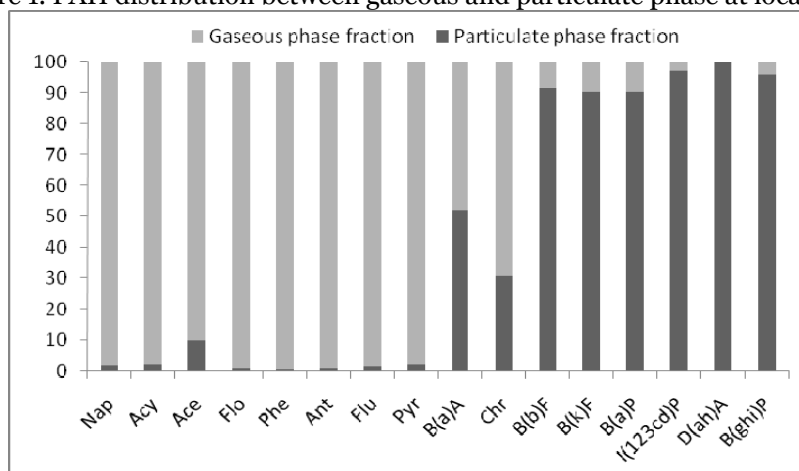


Figure 2. PAH distribution between gaseous and particulate phase at locality P2

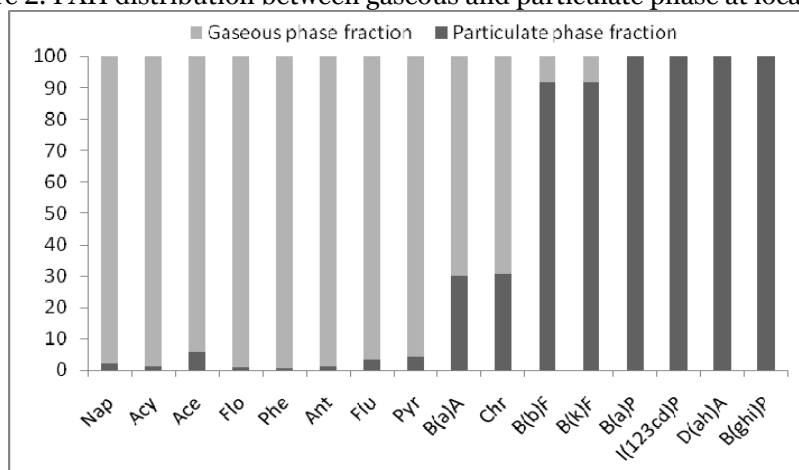


Figure 3. PAH distribution between gaseous and particulate phase at locality P3

In the city of Novi Sad, the highest total concentration level of examined PAHs was detected on the locality P2 (Petrochemical complex Pancevo) and equals $\Sigma\text{PAH}=47.456 \text{ ng/m}^3$. Total concentration of PAHs at the localities P1 (oil refinery) and P3 (city center) are $\Sigma\text{PAH}=26.036 \text{ ng/m}^3$ and $\Sigma\text{PAH}=10.747 \text{ ng/m}^3$, respectively.

In national legislation, maximum allowed concentration of examined group of persistent organic pollutants has not been defined, therefore comparison with legally adopted values was not possible. Threshold value of ambient air quality for benzo(a)pyrene for 24-hour sample, 0.1 ng/m^3 , has been exceeded at the localities P2 and P3, with value 0.108 ng/m^3 for locality P2 and 0.130 ng/m^3 for locality P3.

Obtained experimental results point out on almost complete particle sorption of pollutants B(b)F, B(k)F, B(a)P, I(1,2,3-cd)P, D(ah)A i B(ghi)P, with exception of sampling site P1 (Oil Refinery

Pancevo), where foregoing PAHs fractions, beside D(ah)A, are about 50%. Specific distribution of polycyclic aromatic hydrocarbons at oil refinery, does not manifest, apriory, low concentration of total suspended particles in the atmosphere. Increased concentration levels of PAHs in gaseous phase or sorbed at ultrafine particles which can not be collected at glass fibre filters, issued from refinery, are probably responsible for atmospheric distribution of PAHs at site P1.

4. CONCLUSIONS

Results of analysis point out on the presence of residual quantities of PAHs in air samples from three localities in the town of Pančevo.

The highest concentrations of examined polycyclic aromatic hydrocarbons was detected at the petrochemical complex (47.456 ng/m³).

Regulation defines limit value of ambient air quality only for benzo(a)pyrene (0,1 ng/m³ for 24-hour sample). Limit value was exceeded at two selected localities in Pančevo – petrochemical complex (0.108 ng/m³) and city center (0.130 ng/m³).

Direct influence of atmospheric distribution on wet and dry deposition processes, long-range transport, as well as potential reactions of degradation of PAHs in the atmosphere, points out on an extreme importance of examination and determination of concentration levels and partition of pollutants in the atmosphere.

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