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Comparison between PAH Mass Concentrations Measured in PM_{10} and $PM_{2.5}$ Particle Fractions

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Polycyclic aromatic hydrocarbons (PAHs) widely distributed pollutants in the atmosphere are product of incomplete combustion of fossil fuels and other organic materials. Their sources include natural processes (forest fires and volcanic eruptions) and anthropogenic emissions (motor vehicles, industrial processes, domestic heating, tobacco smoke and other.

They consist of two or more benzene rings. Most PAHs with fewer rings are gases, while those with more benzene rings bind to particles according to their affinity. Most of them are associated with fine airborne particles which can be taken into the bronhioles and alveoli of the lungs (Katz, 1980). It is generally accepted that PAHs associated with small particles (< 1 μm) tend to result from combustion or other high temperature sources whereas large particles (>10μm) are likely to arise from wind action on soils and deposited dust (Sheu, 1997). This property of PAH size distribution largely determines the degree of penetration of the respiratory system and so is related to human toxicity. Levels of PAHs concentration in the atmosphere depend on residental heating (coal, wood, oil), traffic density, type of industrial emissions, and tend to vary with season and meteorological conditions. More than 500 PAH have been identified in the air, but only 1-20 are measured (Lee, 1981). Several compounds of this group have been classified by the International Agency for Research and Cancer (IARC) as probable (2A) or possible (2B) human carcinogens (IARC, 1987). Many developed countries started to measure PAH concentrations in the atmosphere in the mid-20th century. Benzo-a-pyren (BaP) has been the most commonly measured PAH since it is always present, and this substance was used as an indicator of the carcinogenic hazard in environment pollution.

The purpose of this investigation was to evaluate if there were statistically significant differences between PAH mass concentrations measured in inhalable or "thoracic" (PM_{10}) and respirable or high-risk ($PM_{2.5}$) particle fractions during two different seasons.

MATERIALS AND METHODS

Twenty four air samples were collected at one monitoring site in the Northern part of Zagreb, Croatia by low volume PM_{10} and $PM_{2.5}$ samplers (~50 m^3) for a period of 30 consecutive days in winter (January) and summer (July). Glass fibre filters were used to collect PM_{10} and $PM_{2.5}$ particle fractions. The samples were kept in the deep freeze at -18 °C, in aluminium foil until analysed.

PAH samples were extracted with cyclohexane in an ultrasonic bath for one hour,

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separated from undissolved parts by centrifugation and evaporated to dryness in a mild stream of nitrogen at 30 °C. Then they were redissolved in acetonitrile. A detailed procedure for the preparation of samples has been described earlier (Šišović, 1991). The analysis was performed by Varian Pro Star high-performance liquid chromatograph (HPLC) and a fluorescence detector with changeable excitation and emission wavelength, in order to optimise the selectivity and sensitivity for individual PAH species (Colombini, 1998). For preparation of calibration curves commercial PAH standard (Supelco SS EPA 610 PAHs Mix) was used. Samples were analysed for the following PAHs: fluoranthene (Flu), pyrene (Pyr), benzo-b-fluoranthene (BbF), benzo-k-fluoranthene (BkF), benzo-a-pyrene (BaP) and benzo-ghi-perylene (BghiP).

RESULTS AND DISCUSSION

Figure 1 shows day-to-day variations of four PAHs mass concentrations (Flu, Pyr, BaP and BghiP), measured over 30 consecutive days in PM_{10} and $PM_{2.5}$ particle fractions in winter. Concentrations of PAHs measured in different particle size shows similar daily variations. Day to day variations mainly depend on weather conditions (wind direction, velocity and temperature variations).

The average mass concentrations and other statistically important parameters of PAH measured in PM_{10} and $PM_{2.5}$ particle fractions in winter are shown in Table 1. Pyrene showed the highest average value measured in PM_{10} 4.982 ng/m^3 and the lowest average value of mass concentrations had BkF in $PM_{2.5}$ 2.098 ng/m^3. Average mass concentrations of BaP were 3.093 ng/m^3 in PM_{10} and 3.178 ng/m^3 $PM_{2.5}$. Average mass concentrations of Flu in PM_{10} was 3.905 ng/m^3 and in $PM_{2.5}$ 3.675 ng/m^3. Table 2 shows statistical parameters and difference between PAH mass concentrations (ng/m^3) measured in different particle size in winter.

Table 1. Statistical parameters of mass concentrations PAHs (ng/m^3) measured in PM_{10} and $PM_{2.5}$ in winter.

PAU		N	$C_{min.}$	$C_{max.}$	C	STD	SE
Flu	PM_{10}	30	0.487	10.392	**3.905**	2.6437	0.4827
	$PM_{2.5}$	30	0.409	10.308	**3.675**	2.6118	0.4768
Pyr	PM_{10}	30	0.745	12.379	**4.982**	3.3833	0.6177
	$PM_{2.5}$	30	0.607	12.511	**4.654**	3.0782	0.5620
BbF	PM_{10}	30	0.453	10.332	**3.627**	2.1833	0.3986
	$PM_{2.5}$	30	0.477	9.672	**3.523**	1.9880	0.3630
BkF	PM_{10}	30	0.752	5.596	**2.142**	1.1746	0.2145
	$PM_{2.5}$	30	0.793	5.648	**2.098**	1.1390	0.2080
BaP	PM_{10}	30	0.519	10.122	**3.039**	2.1416	0.3910
	$PM_{2.5}$	30	0.561	12.732	**3.178**	2.4954	0.4556
BghiP	PM_{10}	30	0.865	9.016	**4.081**	2.1591	0.3942
	$PM_{2.5}$	30	0.907	8.398	**4.099**	2.0187	0.3686

N - number of samples
$C_{min.}$ - minimum value
$C_{max.}$ - maximum value
C - arithmetic means
STD - standard deviation
SE - standard error

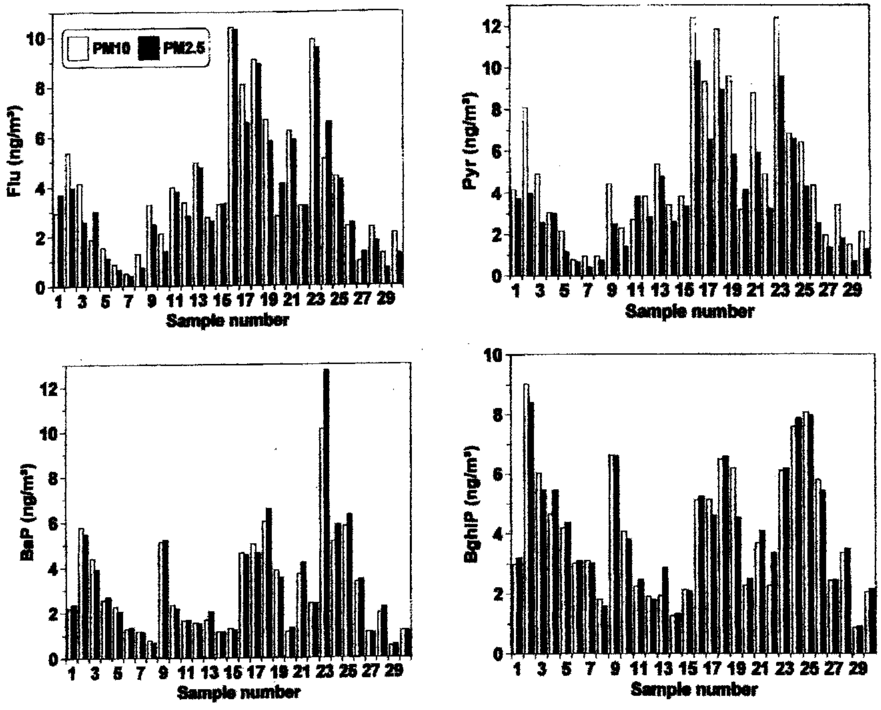

Figure 1. Day to day variations of some PAH mass concentrations measured in PM_{10} and $PM_{2.5}$ in winter.

Table 2. Statistical parameters and significance of difference in PAH mass concentrations (ng/m³) measured in PM_{10} and $PM_{2.5}$ in winter.

PAH	N	C ($PM_{2.5}$)	C (PM_{10})	Δ	STD Δ	SE Δ	t
Flu	30	3.675	3.906	0.231	0.7205	0.1316	1.754
Pyr	30	4.654	4.982	0.328	0.6566	0.1199	2.732
BbF	30	3.523	3.627	0.104	0.4052	0.0740	1.406
BkF	30	2.098	2.142	0.044	0.1439	0.0263	1.679
BaP	30	3.178	3.039	-0.139	0.5368	0.0980	1.420
BghiP	30	4.099	4.081	-0.018	0.4927	0.0900	0.201

N - number of samples
Δ - mean difference
C(PM_{10}) - artihmetic means in PM_{10}
STD Δ - standard deviation of mean difference
C($PM_{2.5}$) - artihmetic means in $PM_{2.5}$
SE Δ - standard error of mean difference

Although the average PAH mass concentrations of all PAHs (except BaP and BghiP) were slightly higher in PM_{10}, the differences were not statistically significant ($P>0.05$) except Pyrene ($P<0.01$). Figure 2 shows day to day variations of four PAH mass concentrations measured in PM_{10} and $PM_{2.5}$ particle fraction in summer. PAH mass concentrations in summer shows similar daily variations, like in winter, but the concentrations levels of all PAHs were much lower.

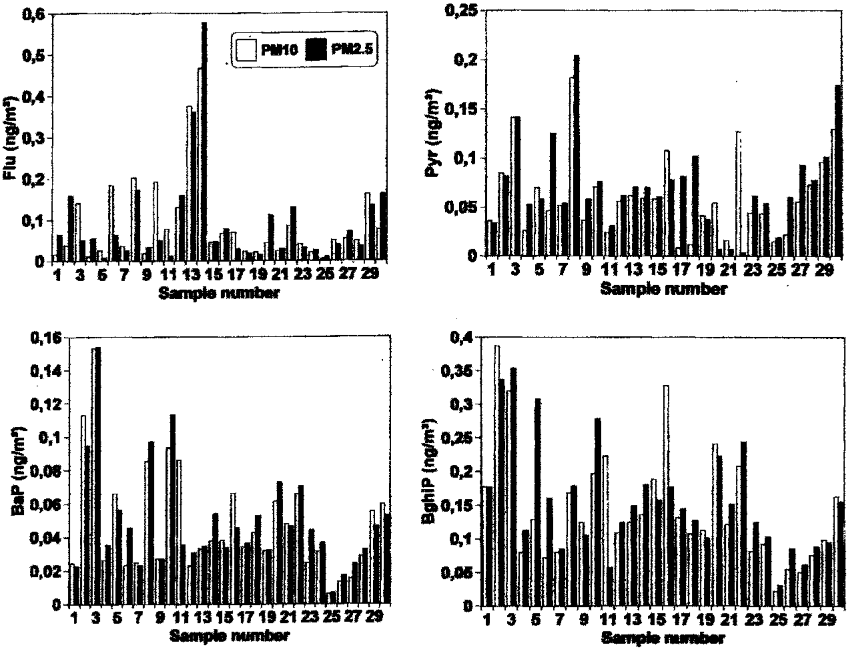

Figure 2. Day to day variations of some PAH mass concentrations measured in PM_{10} and $PM_{2.5}$ in summer.

Summarised results of PAH mass concentrations measured in PM_{10} and $PM_{2.5}$ particle fraction in summer are shown in Table 3.

Table 3. Statistical parameters of mass concentrations PAHs (ng/m^3) measured in PM_{10} and $PM_{2.5}$ in summer.

PAU		N	$C_{min.}$	$C_{max.}$	C	STD	SE
Flu	PM_{10}	30	0.004	0.467	**0.092**	0.1047	0.0191
	$PM_{2.5}$	30	0.008	0.577	**0.092**	0.1158	0.0211
Pyr	PM_{10}	30	0.008	0.181	**0.061**	0.0409	0.0075
	$PM_{2.5}$	30	0.004	0.205	**0.071**	0.0448	0.0082
BbF	PM_{10}	30	0.015	0.235	**0.091**	0.053	0.0097
	$PM_{2.5}$	30	0.019	0.211	**0.094**	0.0439	0.0080
BkF	PM_{10}	30	0.009	0.131	**0.048**	0.0298	0.0054
	$PM_{2.5}$	30	0.008	0.117	**0.050**	0.0267	0.0049
BaP	PM_{10}	30	0.006	0.153	**0.048**	0.0321	0.0059
	$PM_{2.5}$	30	0.007	0.154	**0.049**	0.0306	0.0056
BghiP	PM_{10}	30	0.022	0.387	**0.147**	0.0845	0.0154
	$PM_{2.5}$	30	0.031	0.354	**0.156**	0.0797	0.0146

N - number of samples
$C_{min.}$ - minimum value
$C_{max.}$ - maximum value
C - arithmetic means
STD - standard deviation
SE - standard error

Average mass concentrations levels of all measured PAHs were much lower than in winter. The average mass concentrations of BaP measured in PM_{10} was 0.048 ng/m^3 and in $PM_{2.5}$ 0.049 ng/m^3. The average mass concentration of Flu in PM_{10} and $PM_{2.5}$ were equal 0.092 ng/m^3. The highest concentration of all measured PAHs during summer showed BghiP in $PM_{2.5}$ 0.156 ng/m^3 and the lowest BkF and BaP in PM_{10} 0.048 ng/m^3. Statistical parameters and difference between PAH mass concentrations (ng/m^3) measured in summer are shown in Table 4.

Table 4. Statistical parameters and significance of difference in PAH mass concentrations (ng/m^3) measured in PM_{10} and $PM_{2.5}$ in summer.

PAH	N	C ($PM_{2.5}$)	C (PM_{10})	Δ	STD Δ	SE Δ	t
Flu	30	0.092	0.092	0.0003	0.0574	0.0105	0.0291
Pyr	30	0.071	0.061	0.010	0.0377	0.0069	1.4091
BbF	30	0.094	0.091	0.003	0.0204	0.0037	0.7991
BkF	30	0.050	0.048	0.002	0.0096	0.0018	1.0761
BaP	30	0.049	0.048	0.001	0.0139	0.0025	0.4841
BghiP	30	0.156	0.147	0.009	0.0606	0.0111	0.8394

N - number of samples
C($PM_{2.5}$) - artihmetic means in $PM_{2.5}$
C(PM_{10}) - artihmetic means in PM_{10}
Δ - mean difference
STD Δ - standard deviation of mean difference
SE Δ - standard error of mean difference

Although the average PAH mass concentrations of all PAHs (except Flu) were slightly higher in $PM_{2.5}$, the differences between all were not statistically significant ($P>0.05$).

The average mass concentrations of all measured PAHs in winter (except BaP and BghiP) were slightly higher in PM_{10} than in $PM_{2.5}$ particle fraction, but the differences between the two were not statistically significant. The average mass concentrations of all PAHs in summer were slightly higher in $PM_{2.5}$ (except Flu), but the differences also were not statistically significant. The results of measurements showed that all PAHs were present in respirable (high-risk) particle fractions, regardless of the season. The findings are in good agreement with a number of other findings which showed that BaP and other PAHs, with more benzene rings, are adsorbed on small size particulate matter which directly enters the lower part of human respiratiory system.

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