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PAH MASS CONCENTRATIONS MEASURED IN PM_{10} PARTICLE FRACTION

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ABSTRACT

This paper presents the analysis of PAH mass concentrations measured in PM_{10} particle fraction (PM_{10} particles with aerodynamic diameter less than 10 μm) collected at one measuring site in Zagreb air over four years, and of seasonal differences in PAH mass concentrations in PM_{10} samples collected from 21 March 2003 to 20 March 2004. Twenty-four hour samples were taken in the northern part of Zagreb using a low-volume (50 m^3) sampler with glass fiber filters. The average mass concentrations over four-year measuring period ranged for BaP from 1.17 to 1.87 ng/m^3 and were below the limit value (2 ng/m^3) set by the Ordinance on Recommended and Limit Air Quality Values in Croatia. The highest concentrations of all PAHs measured in PM_{10} samples collected from 21 March 2003 to 20 March 2004 were found in the winter and the lowest in the summer. Mass concentrations of all measured PAHs were much higher in the autumn than in the spring.

Key Words: benzo-a-pyrene, PM_{10}, seasonal variations, limit value

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are widespread compounds generated by incomplete combustion of organic materials. They are emitted from a large variety of industrial processes, motor vehicles and residential heating. Levels of PAH concentrations in the atmosphere vary with season and meteorological conditions. They consist of two or more fused aromatic rings. Some studies showed that PAHs with two or three benzene rings were found to exist in the vapour phase, while PAHs with more than five rings were observed primarily in the particulate phase (Baek, 1992). Most of them are associated with fine airborne particles. It is generally accepted that PAHs associated with small particles (<1 μm), tend to result from combustion or other high temperature sources (Sheu, 1997). More than 500 PAHs have been identified in the air, but only 1-20 are measured (Lee, 1981). Benzo-a-pyrene (BaP) is the most commonly measured PAH since it has been always present and used as an indicator for the carcinogenic hazard in the polluted environment. The natural background level of BaP may be nearly zero, in rural areas the concentration of BaP ranges from 0.01-1 ng/m^3, in urban areas it ranges from 1-10 ng/m^3 and around some industries it goes to 40 ng/m^3 (Guidelines, 2000).

Due to the fact that some PAHs are mutagenic and some carcinogenic, they should not be present in the air, or their concentrations should be the lowest possible. The

concentrations of 2 ng/m^3 for the annual average BaP concentration are the limit value set by the Ordinance on Recommended and Limit Air Quality Values in Croatia (Ordinance, 1996).

This paper presents the analysis of PAH mass concentrations measured in PM_{10} particle fraction (PM_{10} particles with aerodynamic diameter less than 10 μm) collected at one measuring site in Zagreb air over four years and of seasonal differences in PAH mass concentrations in PM_{10} samples collected from 21 March 2003 to 20 March 2004.

2. MATERIAL AND METHODS

Samples were collected at one measuring site in the northern part of Zagreb, Croatia, continuously from 2001 to 2004. Twenty-four hour samples of PM_{10} particles were collected by low volume PM_{10} sampler – Ingenieurbuero Sven Leckel, on glass or quartz filters. Samples were kept in the deep freeze at -18 ˚C, wrapped in aluminium foil until analysed. Samples were extracted with cyclohexane in an ultrasonic bath for one hour, separated from undissolved parts by centrifugation and evaporated to dryness, and redissolved in acetonitrile (Šišović, 1991).

Sample analysis
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. PAH are separated on a Varian Chrompac CP-Eco Spher 4 PAH column. Mobile phase is a mixture of acetonitrile and water and flow rate is 0.4 ml/min. Samples were analysed for the following PAHs: fluoranthene (Flu), pyrene (Pir), benzo-b- fluoranthene (BbF), benzo-k-fluoranthene (BkF), benzo-a-pyrene (BaP) and benzo-ghi-perylene (BghiP).

3. RESULTS AND DISCUSSION

Figures 1-4 show monthly average PAH mass concentrations, and minimum and maximum daily concentrations measured in PM_{10} particle fraction continuously from 2001. The concentrations of all measured PAHs were the lowest during warm period of the year (May, June, July, August). Slightly higher concentrations were measured during March, April, September and October and the highest concentrations were measured during winter months (January, February, November and December). Monthly average BaP mass concentrations, during the warm period of the year, varied from 0.04 to 0.24 ng/m^3, and during the cold season they varied from 2.00 to 5.21 ng/m^3. Concentrations of other PAHs show similar variations during the winter and summer period.

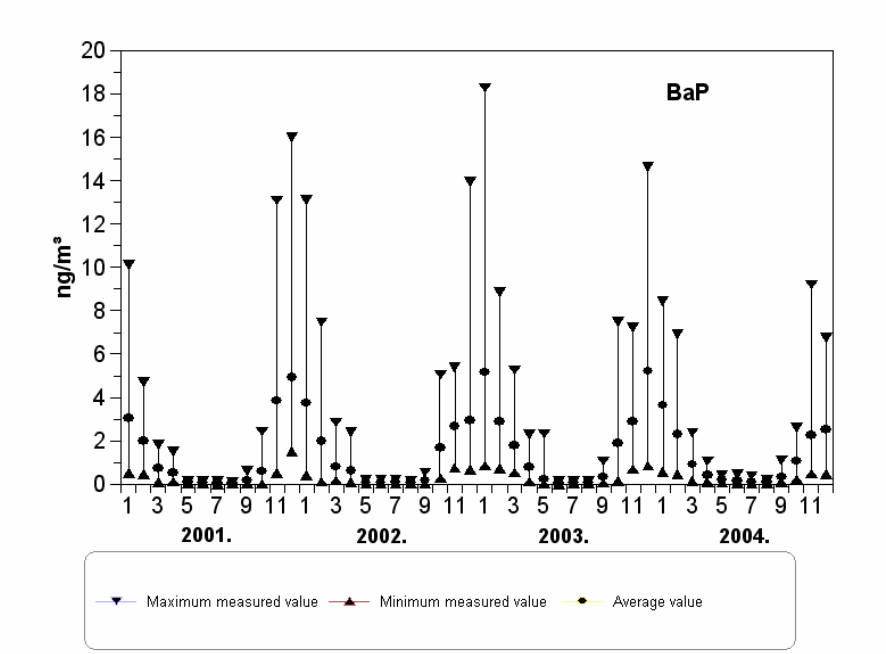

Figure 1 – Monthly average BaP mass concentrations measured during four year period

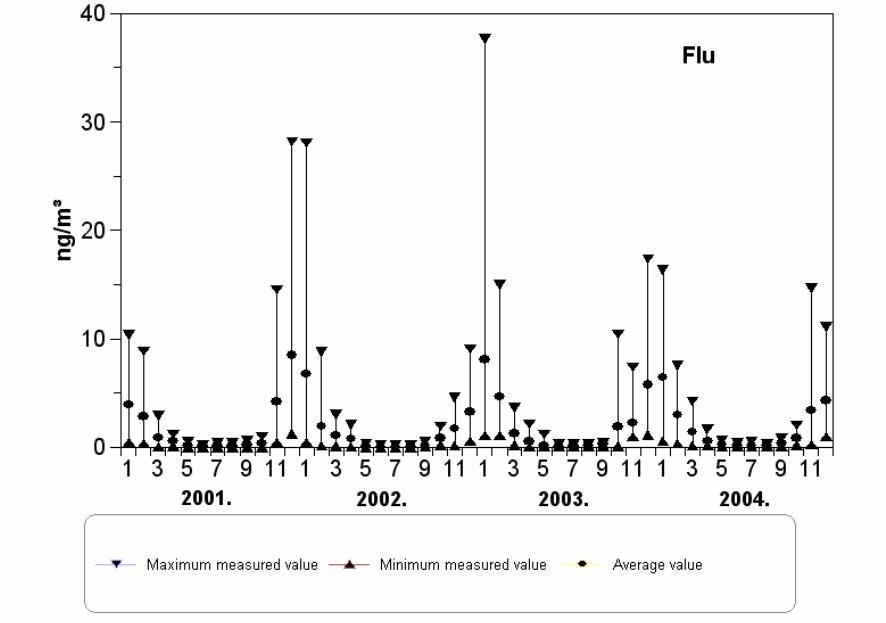

Figure 2 – Monthly average Flu mass concentrations measured during four year period

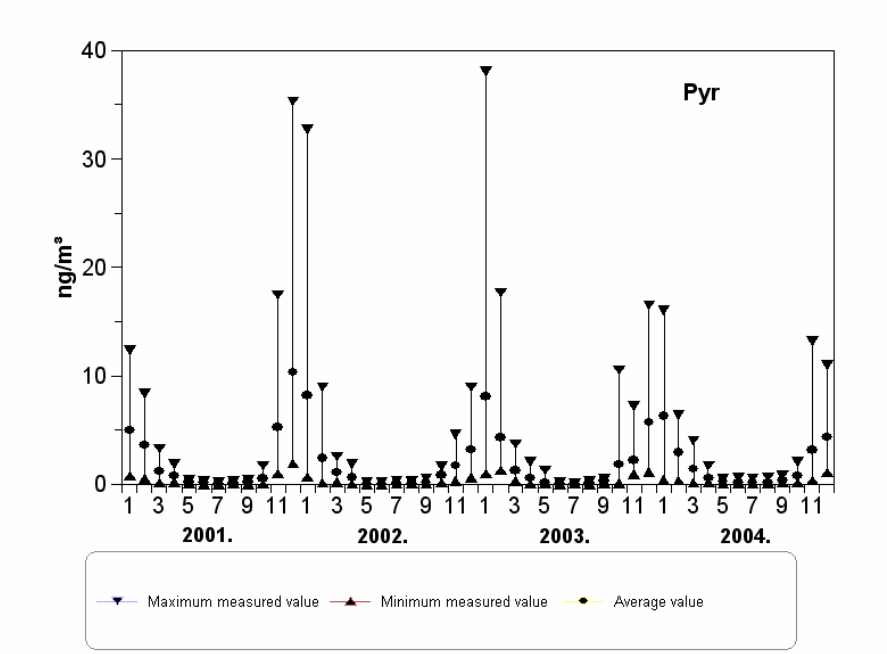

Figure 3 – Monthly average Pyr mass concentrations measured during four year period

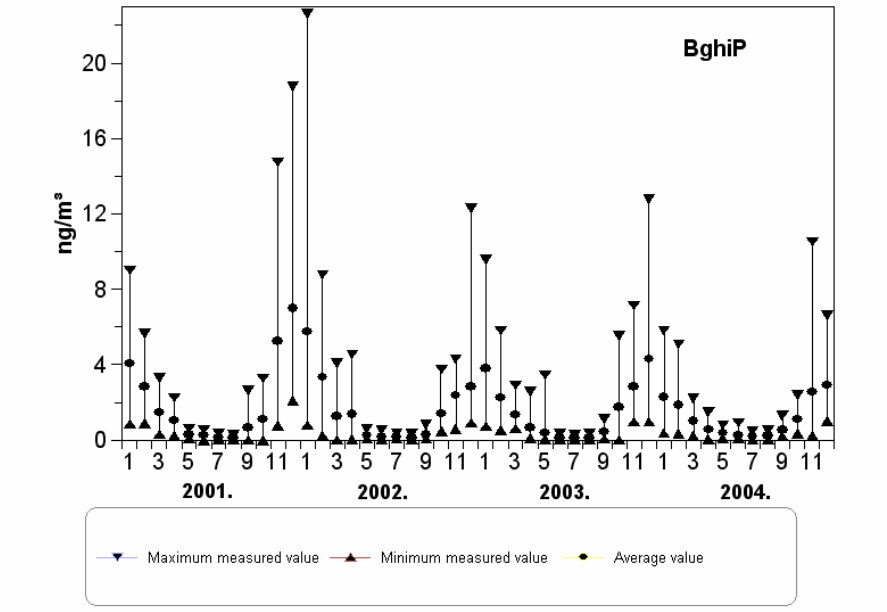

Figure 4 – Monthly average BghiP mass concentrations measured during four year period

Concentrations of Flu and Pyr were higher than those of BaP during the winter months and lower or similar during the summer months. Concentrations of BghiP were similar or higher than BaP in winter, but in summer they were two or three times higher than the concentrations of BaP. Concentrations of PAHs depend on

sources and stability of PAHs during the cold and warm months (Yamasaky, 1982; Greenberg, 1989).

Figure 5 shows daily variations of BaP mass concentrations measured during 2004. Very low concentrations of BaP were found in April and it lasted till September. The highest daily concentration of BaP in 2004 was during November and it was 9.21 ng/m^3. Daily variations of BaP mass concentrations mainly depend on weather conditions (wind direction and velocity).

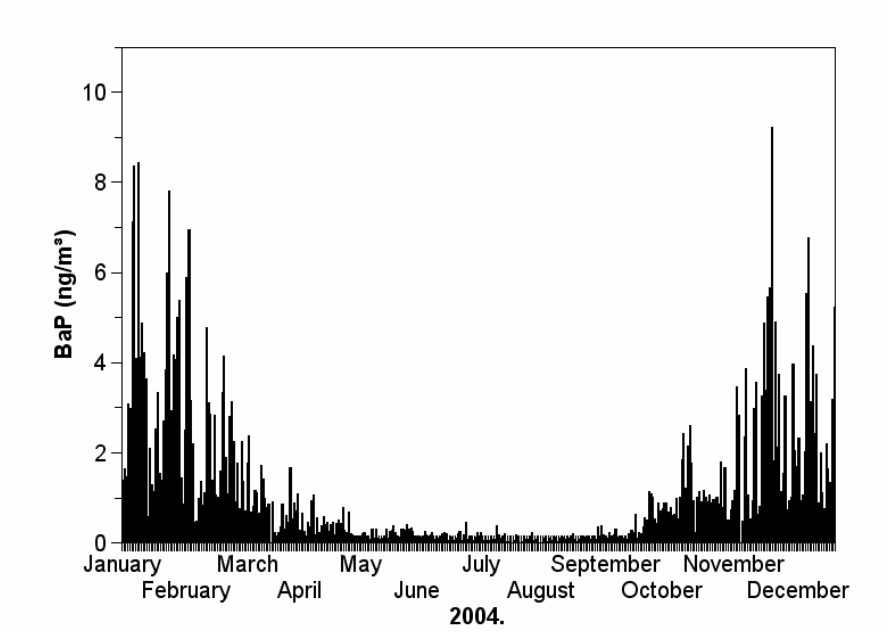

Figure 5 - Daily variations of BaP mass concentrations measured during 2004

In Table 1 are shown the annual average mass concentrations of PAHs (ng/m^3), except for BaP, measured during four-year period. Annual average mass concentrations of Flu and Pyr varied from year to year, and the lowest were in 2002. The concentrations of BbF, BkF and BghiP were the highest in 2001 and after that they went slowly down.

Table 1 - Annual average mass concentrations of PAHs (ng/m^3), except BaP measured at one measuring site during four year period

PAH	2001.			2002.			2003.			2004.		
	N	**C**	C_M	N	**C**	C_M	N	**C**	C_M	N	**C**	C_M
Flu	355	**1.9**	28.2	362	**1.4**	28.1	362	**2.1**	38.7	364	**1.8**	16.4
Pyr	355	**2.3**	35.3	362	**1.6**	32.8	362	**2.06**	38.1	364	**1.7**	16.0
BbF	355	**1.5**	11.2	362	**1.2**	13.3	362	**1.20**	9.9	364	**1.1**	8.5
BkF	355	**0.9**	6.8	362	**0.7**	7.3	362	**0.63**	5.3	364	**0.6**	4.4
BghiP	355	**2.1**	18.8	362	**1.6**	22.6	362	**1.53**	12.8	364	**1.2**	10.5

Table 2 shows annual average BaP mass concentrations measured during a four-year period. The highest annual average value was in 2003 and it was 1.79 ng/m^3 and the lowest was in 2004 and it was 1.17 ng/m^3. The obtained results show that the annual average value for BaP mass concentrations measured during four-year period were higher than the recommended value (0.2 ng/m^3) and lower than limit value (2 ng/m^3) proposed by Croatian law. It can be concluded that the air around the measuring sites regarding BaP was in the 2nd category.

Table 2 - Annual average value of BaP mass concentrations (ng/m^3) measured during four year period

Year	N	**C**	C_{98}	C_M
2001.	355	**1.37**	8.66	15.99
2002.	362	**1.24**	6.95	13.95
2003.	362	**1.79**	9.28	18.28
2004.	364	**1.17**	5.96	9.21

N – number of samples **C – arithmetic means** C_m . minimum value
C_{98} – 98 percentile C_M – maximum value

Table 3 shows seasonal variations of PAH mass concentrations in PM_{10} particles collected from 21 March 2003 to 20 March 2004. The highest concentrations of all measured PAHs were in winter and the lowest in summer. Flu and Pyr had the highest concentrations in winter and they were about 4.2 ng/m^3. Average mass concentration of BaP in winter was 2.94 ng/m^3 and it was lower than those measured earlier. Average mass concentration of BaP in summer was 0.118 ng/m^3 and it was higher than those measured earlier (Šišović, 2002).

Table 3 - Arithmetic means and ranges of PAH mass concentrations (ng/m^3) measured during four seasons

Season	Statistical parameters	PAH (ng/m^3)					
		BaP	Flu	Pyr	BbF	BkF	BghiP
Spring	N	91	91	91	91	91	91
	C	**0.58**	**0.41**	**0.41**	**0.44**	**0.22**	**0.55**
	C_m	0.01	0.03	0.02	0.02	0.02	0.02
	C_M	3.31	3.65	3.71	1.45	1.45	3.48
Summer	N	92	92	92	92	92	92
	C	**0.12**	**0.13**	**0.12**	**0.12**	**0.06**	**0.19**
	C_m	0.01	0.02	0.01	0.02	0.01	0.02
	C_M	0.71	0.49	0.53	0.64	0.31	0.99
Autumn	N	89	89	89	89	89	89
	C	**2.76**	**2.73**	**2.68**	**1.79**	**0.94**	**2.59**
	C_m	0.06	0.08	0.08	0.09	0.04	0.10
	C_M	10.45	15.30	15.10	6.71	3.43	8.18
Winter	N	90	90	90	90	90	90
	C	**2.94**	**4.22**	**4.17**	**2.34**	**1.23**	**2.16**
	C_m	0.16	0.17	0.13	0.12	0.06	0.24
	C_M	14.62	16.38	16.03	8.09	4.32	12.81

N –Number of samples **C – arithmetic means**
C_m –minimum value C_M – maximum value

The concentrations of all measured PAHs were much higher in autumn than in spring. The reason for this is that in spring there are more warm and sunny days than in autumn, and that increased reactivity of these compounds at higher temperatures result in their photochemical, thermal and chemical degradation (Butler, 1981; Greenberg, 1989).

4. CONCLUSION

The annual average BaP mass concentrations measured during four-year period were higher than the recommended value (0.2 ng/m^3) and lower than limit value (2 ng/m^3) proposed by Croatian law. It can be concluded that the air around the measuring sites regarding BaP was in the 2nd category.
Seasonal variations of PAH mass concentrations show that the highest concentrations of all measured PAHs were found in winter and the lowest in summer. Mass concentrations of all measured PAHs were much higher in autumn than in spring. Seasonal variations mainly depend on differences in temperature, but daily variations on the weather conditions (wind direction and velocity).

REFERENCES

Baek SO, Goldstone ME, Kirk PWW, Lester IN and Perry R. 1992. Concentrations of particulate and gaseous polycyclic aromatic hydrocarbons in London air following a reduction in the lead content of petrol in the United Kingdom. Sci Total Environ. Vol. 111, pp 169-199.

Butler J.D. and Crossley P. 1981. Reactivity of polycyclic aromatic hydrocarbons adsorbed on soot particles. Atmos. Environ. Vol. 15, pp. 91-94.

Greenberg, A. 1989. Phenomenological study of benzo(a)pyrene and cyclopenteno(cd)pyrene decay in ambient air using winter/summer comparison. Atmospheric Environment 23, 2797-2799.

Guidelines for Air Quality, WHO, Geneva, 2000.

Lee, M.L., Novotny, V.M., Bartle, D.K. 1981. Analytical Chemistry of Polycyclic Aromatic Compounds. Academic Press Inc. New York.

Ordinance on Recommended and Limit Air Quality Values, 1996. Official Gazzette No. 101, 4198-4200 (in Croatian).

Sheu H L. et al. 1997. Particle bound PAH content in ambient air: Environmental Pollution. Vol. 96, pp. 369-382.

Šišović A, Fugaš M. 1991. Comparative Evaluation of Procedures for the Determination of PAH in Low-volume Samples, Environ. Monitoring and Assessment. Vol. 18, pp. 235-241.

Šišović A, Škrbec A, Vadjić V. et al. 2002. PAH Levels and Profiles in the Suspended Particulate Matter in Zagreb through Four Seasons. Environmental Monitoring and Assessment. Vol. 74, pp. 217-224.

Yamasaki H, Kuwata K and Miyamoto H. 1982. Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons. Environ Sci Technol. Vol. 16, pp. 189-194.