

## Summertime PAH assembly in Mediterranean air: the Herceg Novi sampling station as an example

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**Abstract:** The results of an analysis of the total suspended particles (TSP), total solvent organic extracts (TSOE), and polycyclic aromatic hydrocarbons (PAHs) in aerosol samples collected from the atmosphere of Herceg Novi from 17th June to 15th September in 1998 and 1999 are presented. The TSP and TSOE concentrations were determined by the standard gravimetric method, whereas the PAHs from the organic part of the aerosol were analysed by the GC-MS method. The difference found in the TSP and TSOE contents between the two consecutive years (before and after the bombing of Yugoslavia) was attributed to changes in the intensity and origin of emissions from dominant sources, specific to the summer period of this region. The content and nature of the PAHs identified in the samples of 1998 and 1999 were also different, indicating the significance of traffic as the source of PAHs, which was of significantly lower intensity in 1999 (immediately after the war) due to the lower influx of tourists. Factor analysis showed that the PAH distribution at the measuring site in 1999 was largely determined by meteorological parameters, mainly by the average daily temperature and wind direction. In 1998, the dominant impact on the PAH distribution was attributed to traffic, both local and from a wider region, without an explicit impact of meteorological parameters.

**Keywords:** PAHs, Mediterranean air pollution, particulate matter, meteorological conditions, factor analysis.

### INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds formed during incomplete combustion or/and pyrolysis of organic materials. They can be released into the atmosphere from both natural and anthropogenic sources, but their occurrence in ambient air seems to be mainly of man-made origin (*i.e.*, coal, oil and gas combustion facilities, motor vehicles, waste incineration and industrial activities).<sup>1,2</sup> The con-

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tribution of natural sources to PAH concentrations are limited, being restricted to spontaneous biomass combustion and volcanic emissions.<sup>3</sup> Due to their low natural emission, PAHs are good tracers of anthropogenic inputs into the atmosphere. Although often associated with urban and industrial zones, they can also be found in rural,<sup>4</sup> well as remote<sup>5</sup> or even marine regions,<sup>6</sup> because of their relatively high persistence in the environment and their ability to be transported over long distances.

The scientific interest in the study of PAHs is expected to become even more widespread in Europe in the next few years, since the recently adopted 4th European Daughter Directive on Air Quality<sup>7</sup> requires long term assessment of particle-bound contaminants. Special attention shall be focused on PAHs of carcinogenic concern IRAC,<sup>8</sup> known to be mostly associated with the particulate phase. Therefore, it is of importance to understand the abundance, distributions and potential sources of PAHs in order to establish air quality standards and to ensure the safety of humans and ecosystems. Hitherto, detailed air pollution studies related to these species in Serbia and Montenegro (SCG–former Yugoslavia) have been scarce.

The results presented in this paper are based on summertime measurements (1998 and 1999) of ambient suspended particulates at a suburban site of the town of Herceg Novi (Adriatic coast of Montenegro). It was deemed interesting to investigate the characteristics of air pollution with respect to PAHs in the chosen period, bearing also in mind the possible consequences of the bombing of Yugoslavia from 24th March to 10th June 1999.

In a suburban environment, such as the area investigated, the dominant pollution sources are emissions from traffic and biomass combustion, since there is no domestic heating in the summer. However, the pollution features affected by local sources may be greatly modified by meteorological conditions, thus changing the abundance of specific PAHs in aerosols. Since the weather in this area (as part of the complex Mediterranean Basin) is in summertime under the effect of the drought-dominated subtropical Azores anticyclone,<sup>9</sup> which allows long residence times of aerosol particles in the atmosphere, the location of Herceg Novi may also behave as a receptor of anthropogenic emissions by long- and medium-range transport. The purpose of this investigation was, therefore, also to assess the effect of meteorological conditions on the abundance of specific particle-bound PAHs.

#### AREA DESCRIPTION AND METEOROLOGICAL CONDITIONS

The town of Herceg Novi (18° 33' N, 42° 27' E) is situated in south-west Montenegro, at the entrance to the Boka Kotorska, the biggest gulf in the Adriatic Sea (Fig. 1). The gulf is composed of several smaller broad bays, connected by relatively narrow channels. In the immediate hinterland of Boka Kotorska, the Dinaric Mountains are lying in the NW-SE direction (*e.g.*, the peaks of Orjen 1894 m and Lovćen 1749 m)<sup>10</sup> with significant impacts on the air circulation and rainfall in this area. Owing to its attractive geographic location, the city of Herceg Novi with its outskirts (*ca.* 42 000 inhabitants) is an important tourist destination, hence

the population is substantially increased in the summer period. This effects the traffic density (road and marine) and other residential activities, which result in increased PAH (and other pollutants) emissions into the atmosphere.

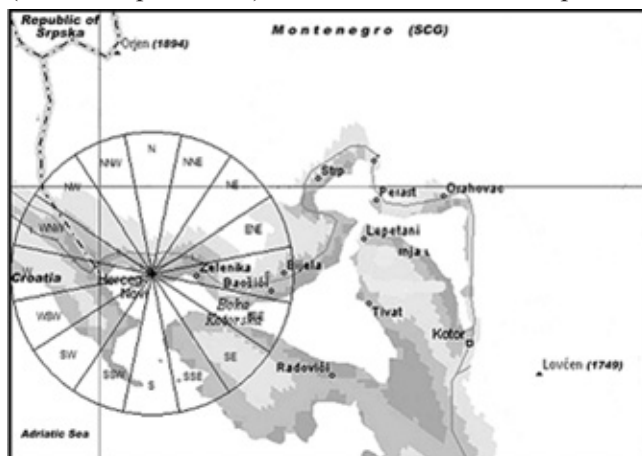


Fig. 1. Map of the studied area showing the sampling site.

The narrow coastal belt of Boka Kotorska appertains to the Mediterranean climatic zone, the main characteristics of which are dry weather and sparse rainfall during the summer. The high number of sunny hours results in relatively high average air temperatures, with maxima in July and August (Herceg Novi around 25 °C). The relative air humidity is around 70 %. Although the winds are often variable, the prevailing directions in the summer are SE/S/SW.<sup>10</sup>

## EXPERIMENTAL

### *Sample collection*

A total of 32 available aerosol samples were analysed. Sixteen samples were collected from 17th June to 15th September 1998, while the other sixteen were collected from 17th June to 15th September 1999. The sampling equipment was located on the rooftop of the meteorological station building in the eastern suburb of Herceg Novi (Fig. 1). This sampling site is included in the network for monitoring airborne pollutants along the Mediterranean coast.<sup>11</sup> The height was about 5 m above ground, at a distance less than 15 m from the coast, with no vertical obstacles in between. The nearest traffic thoroughfare is about 100 m away from the measuring site. There is no major industrial activity in the area and the site is exposed to municipal emissions.

Sampling of the total suspended particles (TSP) was carried out using a high volume sampler AQUERO, model 400XT, equipped with holders for glass-fiber filters (Schleicher & Schuell, 20 x 25 cm, type GF 6). The flow rate was set at 50 m<sup>3</sup> h<sup>-1</sup> and operation time was 24 h, commencing at 9:00 AM. The sampling frequency was 1-in-6-days. The meteorological parameters (temperature, relative humidity, wind direction and velocity) were measured during TSP sampling.

### *Quantification of the TSP*

Determination of the content of TSP is described elsewhere.<sup>12</sup> Briefly, the content of TSP was quantified gravimetrically. The sensitivity of the balance was 0.01 mg. Quality control was provided by simultaneous measurements of three filter blanks, which were kept together with the samples.

#### *Analysis of the organic part of the TSP*

Total solvent organic extracts (TSOE) were recovered from the filter material by ultrasonic agitation, which has been reported to give higher recoveries of PAHs than Soxhlet extraction.<sup>13</sup> The filter paper (third-sheet) was cut into small pieces and extracted ultrasonically 4 times using 30 ml aliquots of dichloromethane, which was of analytical grade quality and redistilled in an all-glass distillation apparatus. Each extraction lasted 15 min at room temperature. The extracts were dried over anhydrous sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) and then filtered. The resultant filtrates were combined and concentrated to a volume of approximately 1 ml using a rotary evaporator (bath temperature  $\leq 30$  °C). The total extracts were transferred to a pre-weighted 5 ml conical vial and the solvent evaporated under a stream of nitrogen gas.

#### *Quantification of the TSOE*

The extracts were quantified gravimetrically. A procedure blank was also performed.

#### *GC-MS analysis*

All the samples were analysed using gas chromatography (Agilent 6890) with mass selective detection (Agilent 5973) operated in the electron impact mode (70 eV) and equipped with an automatic sampling system. The separation of the compounds was carried out through an Agilent 19091S HP-5MS capillary column (30 m). The chromatographic conditions were as follows: injector temperature, 280 °C; ion source temperature, 180 °C; temperature program: 50 °C (5 min), 50–290 °C at a rate of 6 °C  $\text{min}^{-1}$ , 290 °C (15 min). The carrier gas was helium at a constant flow rate of 1.0 ml  $\text{min}^{-1}$ . The total run time for each sample was about 60 min.

Data acquisition and processing were based on a HP Chemstation Data System and Amdis 32 software for the GC-MS, combined with the retention indices and mass spectra published in the literature. Some PAHs which were difficult to separate by gas chromatography and were of identical quality were presented as the total amount of the isomer and one of the isomers was used as a standard because of their identical responses to the flame ionization detector.<sup>14,15</sup>

#### *Quality control*

Operational blanks (unexposed filters) were used simultaneously with field samples. Method blanks (solvent) were also analysed. PAHs were not detectable in either.

## RESULTS AND DISCUSSION

### *General aerosol characteristics*

The samples collected during rainy days (four samples in 1998 and three samples in 1999) were not taken into consideration for reasons of consistency. The total numbers of samples processed and some basic characteristics of the analysed aerosols are presented in Table I.

The concentrations of the TSP and TSOE given in Table I are comparable with those reported in the literature for samples from some rural and semiurban localities in the Mediterranean region, sampled by the same method.<sup>17,18</sup> However, the literature data cannot be correlated with the observed differences between the concentrations of TSP and TSOE for the samples from 1998 and those from 1999. Such concentration differences were recorded in studies dealing with seasonal variations or are characteristic to some individual measuring sites, which was not the present case, since the samples were taken in the same period of the year in two consecutive years at the same location, without substantial differences in the mete-

orological parameters (Table I). Such a difference can be accounted for by the characteristics of the sampling site. Namely, semiurban and rural areas are prone to variations in intensities of local sources, meteoroparameters and air mass movements.<sup>17</sup> Consequently, the TSP concentrations reflect changes in the dominant sources and meteorological parameters, and it is in these factors that the causes of the situation should be sought.

TABLE I. General characteristics of the samples and meteorological data

		Summer 1998 ( $n = 12$ )		Summer 1999 ( $n = 13$ )	
		Range	Mean	Range	Mean
TSP	[ $\mu\text{gm}^{-3}$ ]	39.59 – 94.04	$66.87 \pm 20.27$	14.13– 104.54	$32.36 \pm 23.71$
TSOE	[ $\mu\text{gm}^{-3}$ ]	4.02 – 11.35	$6.46 \pm 2.16$	0.95 – 4.48	$1.79 \pm 0.99$
TSOE/TSP	[%]	8.06 – 13.28	$9.73 \pm 1.66$	4.29 – 7.52	$5.91 \pm 0.91$
LMW PAH	[%]	26.14 – 52.75	$35.82 \pm 8.40$	41.45 – 100.00	$64.43 \pm 25.44$
HMW PAH	[%]	47.25 – 73.86	$64.18 \pm 8.40$	0.00 – 58.55	$35.57 \pm 25.44$
$T$	[°C]	22.00 – 28.70	$25.55 \pm 2.56$	21.20 – 27.90	$24.23 \pm 1.77$
$RH$	[%]	46.71 – 76.70	$65.47 \pm 8.50$	54.71 – 80.00	$69.40 \pm 8.46$
$Max.W$	[ $\text{ms}^{-1}$ ]	4.50 – 12.52	$6.53 \pm 2.29$	4.20 – 10.40	$6.86 \pm 1.89$

$n$  – Number of samples considered; LMW PAH – low molecular weight PAH are those with  $\log p_L^\circ$  higher than -5 Torr at 20 °C; HMW PAH – high molecular weight PAH are those with  $\log p_L^\circ$  lower than -6 Torr at 20 °C;  $T$  – average daily temperature;  $RH$  – relative humidity;  $Max.W$  – maximum wind gusts

The relatively high standard deviations of the concentrations observed within the two sample groups was explained as being the consequence of using a high throughput sampler, in such a case, fluctuating wind speed and direction cause variations in the sampling of larger particles ( $>5 \mu\text{m}$ ).<sup>19</sup>

#### PAH distributions in the ambient TSP

The GS-MS results showed that PAH species associated with a particle mode comprise the sum of 12 parent compounds included in Fig. 2.

The first feature to be noted is the composition variations between the two sets of samples. In the summer of 1998 (Fig. 2a), the major contributors to the total PAHs were BxF (16.75 %), FLT (14.93 %), PYR (12.94 %), BGP (12.52 %) and the total PAHs are, in general, dominated by HMW PAHs (see Table I), which all indicate the significance of traffic as a dominant source of PAHs, *i.e.*, emission from petrol and diesel engines.<sup>20</sup> (The abbreviations of the PAHs are explained in Fig. 2). According to IARC,<sup>8</sup> several of the PAHs (BaA, BxF, BaP, INP) are suspected carcinogens, thus their presence in suspended particles is of concern. The content of carcinogenic species is, on average, 28 % of the total PAHs.

In the summer of 1999 (Fig. 2b), however, the most volatile LMW PAHs were dominant ( $\approx 63$  % on average) in the relative PAH compositions. The prevalent

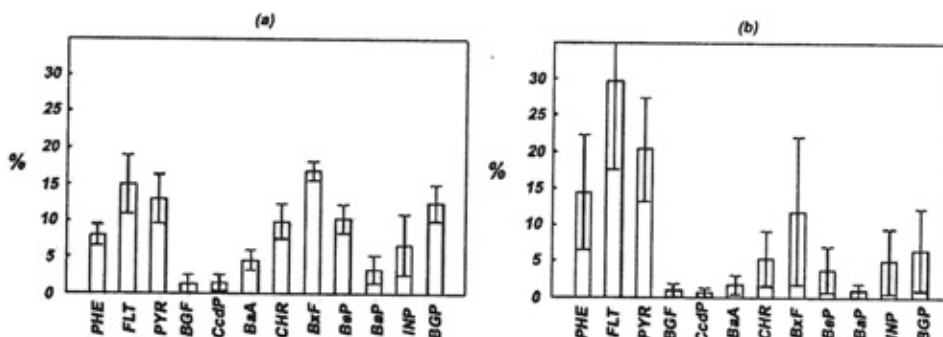


Fig. 2. Average relative PAH composition in the TSP samples collected at Herceg Novi. Error bars correspond to standard deviation. a: Summer of 1998. b: Summer of 1999. Abbreviations: PHE – phenanthrene + anthracene (determined cumulatively as unresolved by gas chromatographic analysis); FLT – fluorethene; PYR – pyrene; BGF – benzo[ghi]fluoranthene; CcdP – cyclopenta[cd]pyrene; BaA – benz[a]anthracene; CHR – chrysene + triphenylene; BxF – benzo(j)fluoranthene + benzo(b)fluoranthene + benzo(k)fluoranthene; BeP – benzo(e)pyrene; BaP – benzo(a)pyrene; INP – indeno[1,2,3-cd]pyrene; BGP – benzo[ghi]perylene.

PAHs were FLT (29.77 %), PYR (20.26 %), PHE (14.30 %) and BxF (11.78 %). The contribution of carcinogenic PAHs ( $\approx 20$  % on average) was lower than in the summer of 1998.

Student's *t* test was performed on the ratios of the individual PAHs in the two groups of samples. The results revealed a statistically significant difference in the ratios for the individual PAHs of the sets of samples at the 0.01 level. The differences in composition indicate that particle associated PAHs in the two summertime sets have different origins or succumb to affects of different meteorological parameters.

In order to determine whether and to what extent the meteorological parameters affect the distribution of PAHs throughout the analysed period, Factor Analysis with principal component extraction was performed using the SPSS 10.0 statistical package.

#### Factor analysis

Factor analysis (FA) has been proven to be an effective statistical tool in analysing data trends and relationships.<sup>21</sup> In principle, FA is a data reduction technique. The scope of the FA is to group chemical species according to the similarities of variations and to assign physical and chemical significance to these groups.

The twelve PAH species, TSP, TSOE, and four meteorological parameters (temperature, relative humidity, wind direction and velocity) measured at the sampling site were subjected to FA with VARIMAX rotation. According to the Kaiser criterion, only those factors corresponding to eigenvalues  $>1$  were retained, as shown in Table II. The total percentages of variance explained by the four factors were 87.14 % and 88.73 % for 1998 and 1999, respectively.

TABLE II. Factor analysis results of summertime samples from the Herceg Novi sampling station

	Summer of 1998				Summer of 1999			
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 1	Factor 2	Factor 3	Factor 4
TSP	0.26	<b>0.92</b>	-0.14	-0.01	-0.26	-0.10	<b>0.91</b>	0.11
TSOE	0.04	<b>0.93</b>	0.03	-0.07	-0.34	0.07	<b>0.89</b>	-0.01
PHE	<b>0.89</b>	0.21	0.11	0.13	0.37	<b>0.90</b>	0.02	0.14
FLT	<b>0.76</b>	0.48	-0.13	-0.08	0.57	0.59	-0.21	0.45
PYR	<b>0.73</b>	0.40	-0.39	-0.04	0.59	<b>0.72</b>	-0.01	0.13
BGF	<b>0.94</b>	-0.02	-0.16	0.12	<b>0.73</b>	0.48	-0.25	0.01
CcdP	<b>0.91</b>	0.17	-0.05	-0.24	<b>0.74</b>	0.46	-0.27	-0.01
BaA	<b>0.82</b>	-0.19	0.13	-0.19	<b>0.81</b>	0.42	-0.29	-0.10
CHR	0.68	0.36	0.26	0.29	<b>0.98</b>	0.18	-0.04	-0.03
BxF	<b>0.89</b>	0.33	-0.13	-0.23	<b>0.96</b>	0.07	-0.02	-0.11
BeP	<b>0.84</b>	0.41	-0.02	-0.25	<b>0.95</b>	0.23	-0.07	0.04
BaP	<b>0.90</b>	0.07	-0.04	-0.11	<b>0.76</b>	0.29	-0.22	0.06
INP	0.69	0.47	0.08	0.12	<b>0.87</b>	0.35	-0.25	0.09
BGP	<b>0.87</b>	0.26	0.08	-0.31	<b>0.92</b>	0.22	-0.25	-0.05
<i>T</i>	0.27	<b>0.85</b>	0.29	-0.12	0.01	- <b>0.73</b>	0.58	0.17
<i>RH</i>	0.12	-0.18	- <b>0.91</b>	0.04	0.23	0.16	0.39	<b>0.75</b>
<i>Max. W</i>	0.11	-0.09	<b>0.86</b>	0.39	0.21	0.11	0.06	- <b>0.87</b>
<i>Dir. W*</i>	-0.24	-0.12	0.21	<b>0.92</b>	0.31	<b>0.79</b>	0.13	-0.13
Initial Eigenvalue	9.94	2.51	2.20	1.04	10.57	2.29	1.72	1.39
% Variance	55.23	13.94	12.22	5.76	58.71	12.74	9.56	7.73
Cumulative %	55.23	69.17	81.38	87.14	58.71	71.45	81.01	88.73

Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaiser Normalization; Eigenvalue > 1; Factor loadings > 0.70 are in bold; \*Directions of maximum wind gusts

*Factorial analysis of the data for the summer of 1998.* As can be seen from Table II, Factor 1 (F-1) accounts for 55.23 % of the data variance and includes exclusively PAHs with loadings from 0.68 to 0.94. One part of the PAHs is also in correlation with Factor 2 (F-2), whereas PYR is, with a low loading (-0.39), negatively correlated with Factor 3 (F-3) as well. Factor 2 accounts for 13.94 % of the variance and is characterised by TSP, TSOE, and the average daily temperature (*T*). The PAHs included in this factor are FLT, PYR, BeP, and INP with relatively low loadings from 0.40 to 0.48. Factor 3 and Factor 4 account for 12.22 % and 5.76 % of the variance, respectively. They are characterised by meteoroparameters: relative humidity (*RH*) and maximum wind gusts (*Max. W*) in the third, and the directions of the maximum wind gusts (*Dir. W*) in the fourth factor.

It follows that there are two groups of PAHs.

*Group A* (57.7 % of the total) includes eight PAHs: PHE, BGF, CcdP, BaA, CHR, Bx<sub>F</sub>, BaP and BGP. All, except PHE, belong to the HMW PAHs. The PAHs of Group A, thus, represent a general characteristic of summertime PAH pollution, which is in agreement with the statement that the summer of 1998 was dominated by HMW PAHs, characteristic for emissions from diesel and petrol engines. The association of PHE with BGP and Bx<sub>F</sub>, is also considered to be characteristic of diesel emissions.<sup>22,23</sup> On the other hand, the presence of CcdP and BGF, low BaP, as well as HMW PAH domination, are characteristic for vehicles with petrol engines without a catalyst,<sup>20</sup> common in the wider neighbourhood of the sampling point. In any case, this association of PAHs is characteristic mostly for road traffic emissions. Their relative abundance is not correlated with the TSP in the air (F-2), with the TSOE (F-2), or with meteoroparameters: *T* (F-2); *RH* and *Max. W* (F-3); and *Dir. W* (F-4). Group A of the PAHs is not correlated with the first three meteoroparameters, since these parameters are mainly indicators of the local conditions, whereas no correlation with *Dir. W* can be found due to the frequent variations of the wind direction. It can thus be concluded that they were primarily brought in from a distance and the wider neighbourhood of the measuring site.

*Group B* includes four PAHs, both low-molecular (FLT, PYR) and high-molecular ones (BeP, INP), and correlates with components F-2 (TSP, TSOE and *T*) with relatively low loadings (0.40 to 0.48). In addition, PYR is also negatively correlated with F-3 (−0.39). These PAHs should have various origins, mainly local but also distant sources, due to their simultaneous correlation with F-1. The positive correlation of TSP, TSOE and PAHs from this group with *T* is a consequence of the region characteristics: in summer, when the air temperature is at a maximum, the tourist season is at its peak, meaning that the traffic density is at its highest. All these result in locally increased TSP emission. Also, in this period, the atmosphere of the region receives greater quantities of TSP, TSOE, and PAHs by resuspension, due to an increased evaporation of organic material and a lower stickiness of surfaces. However, since the greatest part of the organic material in TSOE is of biogenic origin, the greatest part of the PAHs does not correlate with TSP and TSOE.<sup>15</sup>

Within the PAHs of Group B, PYR has a negative correlation with a F-3 (−0.39), determined by *RH* (−0.91) and *Dir. W* (0.86), meaning that its abundance is probably associated with winds from the NW to SE directions, *i.e.*, from the wider Boka Kotorska region. The reciprocal dependence on *RH* indicates a decrease in resuspension of the material under the influence of humid winds from the sea.

It can be concluded that during the summer of 1998, the dominant air pollution source at the outskirts of Herceg Novi was traffic, both local and wider regional. Meteorological conditions did not play an explicit role in the distribution of particle-bound PAHs. The particle concentration in the air, as well as the concentration of extractable organic substance is apparently dependent mainly on the local conditions.



*Factor analysis of the data for the summer of 1999.* Factor 1 (Table II) accounts for 58.71% of the variance. This factor is characterised exclusively by PAHs, like in the case of the summer of 1998. Nine PAHs: BGF, CcdP, BaA, CHR, BxF, BeP, BaP, INP and BGP show high loadings ( $> 0.70$ ). Among them, BGF, CcdP, BaA and INP also correlate with F-2, with loadings of 0.35 to 0.48. In addition to the nine mentioned PAHs, F-1 are also characterised by FLT and PYR with more moderate loadings (0.57 – 0.59), which are also relatively significantly correlated with F-2. The correlation of F-1 with *Dir.W* (0.31) and TSOE (–0.34) is weak, pointing to a possible very weak association of these PAHs with the wind direction and organic extract concentration.

Factor 2 accounts for around 13 % of the variance and is characterised by *Dir.W* (0.79), average daily temperature (– 0.73), as well as LMW PAHs: PHE (0.90) and PYR (0.72). FLT, BGF, CcdP, BaA and INP have loadings from 0.35 to 0.59. It follows that the abundance of PAHs in the air which correlate with F-2 explicitly depended on the meteorological parameters *T* and *Dir.W*.

Factor 3 accounts for 9.56 % of the variance and is characterised by TSP (0.91) and TSOE (0.89). *T* and *RH* are correlated with F-3 with lower loadings of 0.58 and 0.39, respectively. The abundance of none of the PAHs is not correlated with this factor. This feature shows that the compositions of particulate matter as well as of the TSOE were quite variable. In addition, it can be proposed that the concentrations of TSP and TSOE in the air depended partly on *T*, probably for the same reason as in the summer of 1998. The statistically significant lower average TSP concentration in this period,  $32.4 \mu\text{g m}^{-3}$ , in comparison to the summer of 1998,  $66.9 \mu\text{g m}^{-3}$  (Table I), indicates a significantly weaker source of particles in the summer of 1999.

Factor 4 accounts for 7.73 % of the variance and is characterised by meteorological parameters: *RH* (0.75) and *Max.W* (–0.87). Only FLT of the PAHs correlates with F-4, with a relatively low loading of 0.45.

The results show that the PAHs can be divided into 3 groups: group A and two B subgroups.

*Group A* (34.7 % of the total PAHs) is defined by CHR, BxF, BeP, BaP, INP and BGP, which are significantly correlated only with F-1. As for the meteorological variables, F-1 has a fairly weak but positive correlation with *Dir.W* (0.31), and a weak negative one with TSOE (– 0.34). This leads to the assumption that these HMW PAHs are of mixed origin – local and brought in from more remote sources.

Based on the quality of the correlations with F-1 and F-2 (Table II) two PAH subgroups can be observed in Group B.

*Subgroup B-1* is defined by semivolatile PAHs: BxF, CcdP, BaA (2.6 % of the total) characteristic for petrol engine emissions. The members of this subgroup are significantly correlated with F-1 and relatively significantly (0.40 – 0.50) with F-2, which is characterised by a positive correlation with *Dir.W* (0.79), as well as a significant negative correlation with *T* (–0.73). The positive correlation with *Dir.W* indicates that this

PAH group is brought in mainly from the SW-NW-N directions (open sea, Dalmatian coast, continental hinterland), *i.e.*, almost entirely from a distance.

*Subgroup B-2* consists of LMW PAHs: PHE, FLT, and PYR, which are significantly correlated with F-2, and also relatively significantly and positively with F-1 (Table II). On average, they represent 62.7 % of the total PAHs, and characterise this period, which is in agreement with previous statements. According to Rogge<sup>20</sup> and Hwang,<sup>24</sup> the presence of PAHs with 3 and 4 aromatic rings, such as PHE, FLT and PYR, indicates a domination of emissions from heavy-duty diesel trucks. For this reason the origin of these PAHs is mixed, with a prevailing impact of distant sources.

Overall, it follows that during the summer of 1999, the distribution of pollutants at the measuring site was dominated by meteoroparameters and not by local sources. Among these, the dominant impact on the distribution of PAHs was associated with (i) the average daily temperature, which affects the gas-to-particle partitioning of the semivolatile components, evaporation and the mobility of particulates, and (ii) the wind direction.

#### CONCLUSION

The composition of the PAHs in the atmosphere of the Herceg Novi area during the summer seasons of 1998 and 1999, as well as the contents of TSP and TSOE, were investigated.

The differences observed in the PAH composition for the two summers, as well as in the concentrations of TSP (66.9 and 32.4  $\mu\text{g m}^{-3}$ ) and TSOE (6.5 and 1.8  $\mu\text{g m}^{-3}$ ), were attributed to changes in the intensity and origin of the dominant sources of pollution at the measuring site in the summers of 1998 (before) and 1999 (after the war). The FA results showed that the dominant pollution source of the Herceg Novi environment during the summer of 1998 was traffic, both local and from a wider region, whereas the meteorological conditions showed no explicit impact.

On the other hand, the results for the summer of 1999 showed that the local sources did not have a dominant influence on the distribution of pollutants, which was attributed to a low influx of tourists immediately after the war. Meteoroparameters, primarily the wind direction and average daily temperature, which affects the gas-to-particle partitioning of the semivolatile components, were found to have played a dominant role.

A common feature of both summers and thus a summer characteristic of the state of pollution of the Mediterranean air by PAHs is the presence of all 12 members of the group of PAHs listed in Table II. However, due to the differences in the intensities of the dominant sources, the relative contributions of the individual PAHs were different.

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## ИЗВОД

## ЛЕТЊИ САДРЖАЈ ПАУ У МЕДИТЕРАНСКОМ ВАЗДУХУ: МЕРНА СТАНИЦА ХЕРЦЕГ НОВИ КАО ПРИМЕР

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У раду су приказани резултати анализе укупно суспендованих честица, укупно екстрактабилне органске супстанце и полицикличних ароматичних угљоводоника (ПАУ) у узорцима прикупљеним из атмосфере Херцег Новог у периоду од 17. јуна до 15. септембра 1998. и 1999. године. Концентрације суспендованих честица и екстрактабилне органске супстанце одређене су стандардном гравиметријском методом, док су ПАУ из органског дела аеросола анализирани гасно-масеном спектрометријом. Постојећа разлика између садржаја суспендованих честица и екстрактабилне органске супстанце у анализираном периоду две узастопне године (пре и непосредно после бомбардовања) приписана је променама интензитета и порекла емисија из доминантних извора, специфичних за летњи период овог региона. Садржај и природа идентификованих ПАУ у узорцима из 1998. и 1999. године су такође различити, што је указало на значај саобраћаја као извора ПАУ, који је 1999. године (непосредно после рата), услед мањег прилива туриста, био знатно слабијег интензитета. Резултати факторске анализе показали су да је дистрибуција ПАУ на мерном месту у 1999. години била одређена примарно метеопараметрима, пре свега средњом дневном температуром и правцем ветра, док је у летњој сезони 1998. године, доминантан утицај на расподелу ПАУ имао саобраћај, како локални, тако и из ширег региона, без експлицитног утицаја метеоролошких параметара.

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