DETERMINATION OF PAH CONCENTRATIONS IN THE AIR OF BELGRADE IN SUMMER 1999

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ABSTRACT

Laboratory for Environmental Physics from the Institute of Physics, Belgrade, has been involved in the programme "Determination of PAH concentrations in the Balkans" organized in the period of June to August 1999. Laboratory for Environmental Physics is almost 15 years involved in fundamental, applied and development research in environmental science. Pollution sources, transport and transformation processes of pollutants and their impact on environment have been investigated. Main topics of the research are physical and chemical characterization of aerosols, trace metals determination in dry and wet deposition, suspended particles and vegetation. An automated wet/dry deposition collector was designed and constructed to be used for the trace metal deposition monitoring. Special attention is focused on sampling of particulate matter PM10 and PM2.5 that have been recognized to have the greatest impact on human health. All preparation and sample analysis are performed in class 100 clean room. Significant part of the activities is also related to the study of kinetics of combustion and its environmental effect and also to the development of methods, sensors and devices for monitoring of meteorological data and detection of polluting gases and vapours. In the Institute of Physics, an automated meteorological station has been constructed and installed in the Institute for nuclear science Vinca. A constitutive part of this meteorological station is the software that gives prediction of pollutant spreading. Models for evaluation of long-range air transport have been developed and applied to predict accidental and permanent transboundary transfer of pollutants. The work is a part of an international effort to monitor and control air pollution in the lower troposphere.

Key words: atmospheric pollution, PAH concentration, measurements

INTRODUCTION

During a NATO campaign a huge quantities of hazardous substances were emitted in the atmosphere due to destruction of chemical plants and industries and oil storage facilities in Yugoslavia. Chemicals released in the atmosphere under suitable meteorological conditions could be transported to large distances and releases contained not only conventional air

pollutants but also semi-volatile organic compounds which include dioxins, furans, PCB's and PAH's, all known to be hazardous to health.
In order to estimate the effects of the war in Yugoslavia to the quality of the atmosphere of the neighboring countries in relation to polycyclic aromatic hydrocarbon levels, the project "Determination of PAH in the Balkans" was initiated in the framework of B.EN.A (Balkan Environmental Protection Association) with the head in Thessalonica, Greece. A measurement programme conducted by National Center for scientific Research "Demokritos" University of Athens, Greece included simultaneous measurements in five cities (Thessalonica and Kozani in Greece, Sofia in Bulgaria, Belgrade in Yugoslavia and Skoplje in FYuRofM), with the proposed sampling frequency of a sample per day for three weekly periods during three months (in total 21 samples for each city).
In Belgrade, PAH the Laboratory for Environmental Physics of the Institute of Physics organized measurement programme at the Meteorological Station at Green Hill in the suburban area of Belgrade (Hs = 243 m, $\varphi = 44^0$ 47'N and $\lambda = 20^0$ 32'E). Standard meteorological data (temperature, humidity and wind speed and direction) were obtained from the Weather Service Center of the Meteorological Station. The station is more than 100 m far from the streets with low frequency traffic that has been significantly reduced due to fuel shortages and summer holidays. Samples were collected on glass fiber 50 mm diameter GF 10 filters (Schleicher & Schueller), using constant flow rate samplers (average air flow rate 12 l/min) with opening towards the ground, on site 1m from the sidewall and 4 m above the ground, on the flat roof of the building in the neighboring of Meteorological Station. On the filters there aerosol phases were collected and eventually volatile compounds due to adsorption on retained particles. The air samples were taken in 24-h intervals, from 0800 to 0800 in weekly periods at the end of June, July and August of 1999.
Air samples were sent to the National Center for scientific Research "Demokritos" at the University of Athens for the analysis purposes. After addition of internal standards (Phenanthrene-d10, Pyrene-d10, Chrysene-d12, Perylene-d12), filters were extracted with 30 ml dichloromethane and treated under ultrasonic conditions for 30 minutes. PAH identification and quantification were performed by high-resolution gas chromatography coupled to high-resolution mass spectrometry (Hewlett Packard 6890 GC-MS) in full scanning mode (m/z range 50-282).
PAH concentrations (ng m^{-3}) in 24-h air samples at Green Hill in Belgrade are presented in Table 1.
All PAH compounds with the concentrations below detection threshold value of 0,01 ng m^{-3} are not presented in the Table 1 and total PAHs were determined only for the concentrations higher than detection threshold value.
The average weekly values of PAH concentrations are presented in Table 2. with the standard deviation for (n-1) population in parenthesis.

CONCLUSIONS

The results of the PAH measurements in the air at Green Hill, in the suburban of Belgrade in summer 1999 indicated relatively high concentrations of dibenzo(a,h)anthracene, benzo(b)fluoranthene and benzo(a)pyrene. For dibenzo(a,h)anthracene, that is not occurring in gas phase, statistical data for three years for aerosols are: arithmetic average was 0,057, geometrical average 0,031, minimal concentration 0,005 and maximal concentration 0,340. The concentrations in the air at Green Hill of this highly toxic and carcinogen compound

are found to be in average as high as 0,43. In this period traffic in the Belgrade area was drastically reduced due to fuel shortages and summer holidays. Having in mind PAH half-lives in the environment: minimum of 55 h in air and maximum of 17,000 h in soil, it may be concluded that the presence of some compounds is connected with re-emission from surfaces contaminated during NATO bombing of the oil refinery, and oil depots in Pancevo. About 20,000 tones of crude oil burned out in the last fire of 8 June, which lasted seven days with accompanying dense black plume at a 150 m height.

Table 1. Atmospheric PAH concentrations (ng m^{-3}) in 24-h (08-08) air samples at Green Hill in Belgrade in the summer of 1999.

Compound / Date	Phenanthrene	Fluoranthene	Pyrene	Benzo(a)anthracene	Chrysene	Benzo(b)Fluoranthene	Benzo(e)pyrene	Benzo(a)pyrene	Indeno(1,2,3-c,d)pyrene	Benzo(g,h,i)perylene	Dibenzo(a,h)anthracene	Total PAH
3/24 June	1,11	3,75	3,02	0,50	1,01	1,39	0,55	0,29	0,67	0,11	0,76	13,16
4/25 "	0,46	2,05	1,28	0,19	0,58	0,72	0,30	0,16	0,31	0,06	0,31	6,42
5/26 "	1,43	5,41	4,49	0,74	1,94	2,92	1,21	0,53	1,21	0,32	0,96	21,16*
6/27 "	0,15	1,71	1,30	0,32	0,65	1,22	0,41	0,14	0,41	0,04	0,39	6,74
7/28 "	0,28	0,70	0,32	0,07	0,35	0,47	0,20	0,12	0,23	0,06	0,22	3,03
8/29 "	0,42	1,26	0,61	0,13	0,33	0,52	0,20	0,05	0,21	0,04	0,24	4,02
9/30 "	1,27	1,50	0,82	0,20	0,35	0,63	0,27	0,11	0,27	0,08	0,32	5,80
7/18 July	1,02	1,91	1,19	0,27	0,56	1,03	0,50	0,18	0,49	0,05	0,47	7,67
8/19 "	0,40	1,39	0,87	0,19	0,55	0,87	0,32	0,14	0,37	0,08	0,36	5,55
9/20 "	0,15	0,99	0,74	0,32	0,64	1,09	0,44	0,22	0,41	0,04	0,37	5,42
0/21 "	0,09	2,22	1,77	0,16	0,62	0,96	0,49	0,18	0,43	0,02	0,52	7,47
1/22 "	0,07	0,45	0,34	0,14	0,29	0,49	0,28	0,18	0,37	0,24	0,37	3,20
2/23 "	0,39	0,83	0,45	0,13	0,21	0,36	0,18	0,07	0,18	0,02	0,20	3,02
3/24 "	0,26	1,73	1,01	0,13	0,44	0,55	0,25	0,11	0,21	0,03	0,29	5,01
3/24August	0,82	1,81	1,49	0,30	0,47	0,82	0,41	0,27	0,38	0,10	0,43	7,30
4/25 "	1,38	1,88	1,59	0,25	0,71	1,59	0,64	0,30	0,72	0,13	0,80	9,98
5/26 "	0,64	2,59	1,99	0,53	1,01	2,06	0,79	0,32	0,69	0,13	0,73	11,49
6/27 "	0,10	1,07	0,82	0,51	0,57	0,75	0,31	0,12	0,30	0,10	0,25	4,90
7/28 "	0,12	1,84	1,36	0,37	0,73	1,49	0,56	0,22	0,56	0,13	0,47	7,87
8/29 "	0,45	1,17	0,88	0,27	0,46	1,24	0,47	0,13	0,51	0,11	0,43	6,12
9/30 "	0,01	1,03	0,64	0,16	0,33	1,07	0,37	0,10	0,29	0,06	0,24	4,30

* Maximum concentrations value related to all PAH compounds in air

Table 2. The average weekly values of PAH concentrations at Green Hill

Compound	June 1999 23/24 - 29/30	July 1999 17/18 - 23/24	August 1999 23/24 - 29/30
Phenanthrene	0,73 (0,52)	0,34 (0,32)	0,50 (0,49)
Fluoranthene	2,34 (1,65)	1,36 (0,63)	1,63 (0,57)
Pyrene	1,65 (1,55)	0,51 (0,48)	1,25 (0,48)
Benzo(a)anthracene	0,30 (0,23)	0,19 (0,08)	0,34 (0,14)
Chrysene	0,74 (0,58)	0,47 (0,17)	0,61 (0,22)
Benzo(b)Fluoranthene	1,12 (0,87)	0,76 (0,29)	1,23 (0,46)
Benzo(e)pyrene	0,44 (0, 36)	0,35 (0,13)	0,50 (0,17)
Benzo(a)pyrene	0,20 (0,16)	0,15 (0,05)	0,20 (0,09)
Indeno(1,2,3-c,d)pyrene	0,47 (0,36)	0,35 (0,11)	0,49 (0,18)
Benzo(g,h,i)perylene	0,10 (0,10)	0,07 (0,08)	0,11 (0,03)
Dibenzo(a,h)anthracene	0,45 (0,29)	0,37 (0,11)	0,48 (0,22)
Total PAH	8,64 (6,40)	5,33 (1,83)	7,42 (2,62)