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The Content of High-Molecular Polycyclic Aromatic Hydrocarbons in Urban Air During FIFA World Cup 2018

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Abstract—Polycyclic aromatic hydrocarbons including benzo(a)pyrene have been determined on aerosol particles in air sampled in several cities of the European part of Russia hosting FIFA World Cup 2018. The average monthly concentrations of benzo(a)pyrene (BaP) in none of the samples in June–July 2018 exceeded the maximum permitted concentration. The maximum average monthly concentration of BaP during the observation period has been found in Kazan (station no 8, July – 0.83 ng/m^3). The average concentration of BaP in the considered cities decreased along the series: Kazan (0.45 ng/m^3), Kaliningrad (0.38 ng/m^3), Moscow (0.35 ng/m^3), Saransk (0.32 ng/m^3), Nizhny Novgorod (0.31 ng/m^3), Samara (0.31 ng/m^3), Rostov-on-Don (0.26 ng/m^3), St. Petersburg (0.22 ng/m^3), Volgograd (0.16 ng/m^3), Sochi (0.01 ng/m^3).

Keywords: PAH, air, urban, FIFA World Cup, football, HPLC

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INTRODUCTION

Air quality is among the most important factors determining the nature condition and human health.

The air pollution in large cities is a topical issue. The air pollution is determined by the pollutants income from urban sources and the atmospheric processes affecting their transfer, spreading, and transformation [1].

Monitoring of the air pollution is a part of national program accomplished by the Federal Service for Hydrometeorology and Environmental Monitoring of Russia (Rosgidromet).

Analysis of the air quality in Russian Federation has revealed that benz(a)pyrene is among the major pollutants of urban atmosphere [2]. Benz(a)pyrene is the only priority polycyclic aromatic hydrocarbons (PAH) subject to obligatory monitoring in Russia (maximum permitted concentration MPC 1 ng/m^3) and is included in the list of pollutants covered by national environmental regulation [3, 4]. Evidently, this list will be extended.

High-molecular polycyclic aromatic hydrocarbons (HMPAH) usually include the substances with relatively high molecular mass ($M > 200$), saturated vapor pressure below 10^{-8} kPa, and boiling point above 435°C, containing 4 or more fused aromatic rings. When in atmospheric air, they are usually adsorbed on solid aerosol particles which can be transported in air and, in contrast to PAH with less of the cycles (2 to 3) are less prone to the decomposition, yet exhibiting the highest carcinogenic action and mutagenic activity as well as other toxic properties [5–8].

11 Russian cities hosted the 21st FIFA World Cup (WC-2018) in June 14–July 15, 2018. The population of the hosting cities (except for Sochi, Kaliningrad, and Saransk) exceeds 1 million, they are large industrial, administrative, and traffic centers. Large cities strongly affect the formation of the global PAH level in the atmosphere.

The major sources of air pollutants with PAH include the fuel-energy, metallurgy, petroleum, and machine-building facilities as well as motor transport [5, 7, 9, 10]. The motor transport is the predominant source of PAH in the urban air in summer [11, 12].

The annual course of benz(a)pyrene concentration in Russia reveals the maximum in winter due to the increased operation of the fuel-energy facilities and reduced air transportation [2].

In view of the importance of PAH monitoring in the environment (including air), modern highly sensitive and selective analytical methods are used to do so, such as

Fig. 1. Schematic map of the air sampling during FIFA World Cup 2018: (*1*) Moscow, (*2*) Sochi, (*3*) Kaliningrad, (*4*) Nizhny Novgorod, (*5*) St. Petersburg, (*6*) Kazan, (*7*) Saransk, (*8*) Rostov-on-Don, (*9*) Volgograd, and (*10*) Samara.

gas chromatography with mass spectrometry detection of high-performance liquid chromatography (HPLC) with fluorimetry detection [5, 13, 14].

This study aimed to evaluate the content of HMPAHs in the air of the cities hosting WC-2018 by means of HPLC.

EXPERIMENTAL

Air sampling in the cities hosting WC-2018 (except for Yekaterinburg, Fig. 1) was performed at 39 state monitoring stations run by the local Rosgidromet departments (Table 1) according to the regulations of RD.52.04.186.89 [15].

The monitoring stations were located at different parts of the cities. They included the "urban background" stations in the residential regions, "industrial" ones near the enterprises, and "auto" near the highways. However, that division was somewhat relative, since practically all the considered residential parts were located in the zone of the influence of the industrial facilities and motorways.

The sampling was performed in June-July 2018 via blowing the atmospheric air through AFA-VP-20 aerosol filter at about 100 L/min following the complete (4 times daily) or partial (3 times daily) program accepted by Rosgidromet. The aerosol particles were samples 6 days in a week at either 01, 07, 13, and 19 or 07, 13, and 19. Several meteorology parameters (direction and speed of wind, temperature, humidity, and atmospheric pressure) and the practical volume of air passed through a filter were recorded during the sampling. At the end of each month, the collected filters and the accompanied data were passed to Laboratory no. 3 of the Research and Production Association "Typhoon" for determination of benz(a)pyrene and other high-molecular PAH.

The filters collected during a month were combined, put in a 150–250 mL glass column, and extracted with hexane (up to 200 mL). The extract was evaporated, 1.8 mL of acetonitrile was added, the sample was stirred and analyzed by means of HPLC.

The HMPAH were identified and quantified using HPLC with fluorimetry detection (an RF-20A detector).

Table 1. Air sampling at the national monitoring stations to determine PAH content during FIFA World Cup 2018

City	Monitoring station numbers	Responsible organization
Moscow	1, 2, 18, 20, 21, 23, 34	FGBU Tsentralnoe UGMS
Sochi	4	FGBU Severo-Kavkazskoe UGMS
Kaliningrad	1, 2, 4	Kaliningradskii TsGMS
Nizhny Novgorod	3, 7, 11	FGBU Verkhne-Volzhskoe UGMS
St. Petersburg	1, 2, 4, 6, 7, 8, 10, 12, 27	FGBU Severo-Zapadnoe UGMS
Kazan	4, 5, 6, 7, 8	FGBU UGMS Respubliki Tatarstan
Saransk	3, 5	FGBU Verkhne-Volzhskoe UGMS
Rostov-on-Don	51, 52, 55	FGBU Severo-Kavkazskoe UGMS
Volgograd	3, 35, 36	FGBU Severo-Kavkazskoe UGMS
Samara	7, 8, 11	FGBU Privolzhskoe UGMS

Table 2. Lowest and highest concentrations of HMPAH in the air of cities hosting FIFA World Cup 2018, ng/m^3

City and number of monitoring stations		BaA	CHR	BeP	BbF	BkF	BaP	DBahA	BPL	INP	Total HMPAH
Moscow, $n = 13$	min	0.40	0.21	0.11	0.06	0.09	0.11	0.003	0.19	0.14	1.32
	max	1.3	1.4	1.3	0.49	0.61	0.68	0.04	1.2	0.77	7.68
Sochi, $n = 2$	min	0.01	0.02	0.01	0.005	0.005	0.007	< 0.001	0.01	0.01	0.09
	max	0.02	0.02	0.02	0.02	0.007	0.013	< 0.001	0.03	0.02	0.14
Kaliningrad, $n = 6$	min	0.37	0.35	0.21	0.21	0.15	0.23	0.01	0.28	0.29	2.10
	max	0.77	0.87	0.46	0.43	0.48	0.54	0.03	0.70	0.65	4.88
Nizhny Novgorod, $n = 5$	min	0.64	0.52	0.41	0.09	0.22	0.19	0.01	0.34	0.23	2.81
	max	0.91	0.91	0.70	0.27	0.35	0.42	0.025	0.66	0.52	4.74
St. Petersburg $n = 14$	min	0.34	0.21	0.37	0.05	0.12	0.03	0.002	0.10	0.05	1.71
	max	1.4	1.3	1.1	0.57	0.68	0.57	0.02	0.71	0.59	6.30
Kazan, $n = 10$	min	0.48	0.47	0.28	0.21	0.34	0.19	0.01	0.52	0.29	2.95
	max	1.5	1.7	1.3	0.82	0.82	0.83	0.05	1.4	1.2	9.61
Saransk, $n = 4$	min	0.41	0.42	0.34	0.11	0.13	0.19	0.01	0.31	0.21	2.15
	max	1.0	1.4	1.3	0.32	0.47	0.60	0.04	0.90	0.75	6.78
Rostov-on-Don, $n = 6$	min	0.40	0.07	0.25	0.16	0.14	0.13	0.004	0.23	0.19	1.77
	max	1.5	1.7	1.1	0.62	0.57	0.46	0.04	1.0	0.94	7.93
Volgograd, $n = 5$	min	0.17	0.19	0.26	0.01	0.05	0.03	0.006	0.08	0.06	1.08
	max	0.56	0.48	0.57	0.19	0.20	0.24	0.02	0.43	0.35	2.67
Samara, $n = 6$	min	0.32	0.15	0.17	0.07	0.08	0.10	0.006	0.12	0.12	1.14
	max	1.0	1.1	0.81	0.41	0.44	0.53	0.03	0.65	0.60	5.45

The measurements were performed using an LC-20 Prominence chromatograph (Shimadzu), equipped with a DGU-20A$_3$ vacuum degasser, an LC-20AD pump, a SIL-20A autosampler, a CTO-20A thermostat, a SUPELCO-SIL LC-PAH column (150×4.6 mm, 5 μm), a C18 protective cartridge (4×2 mm) (Phenomenex) under conditions of gradient elution with acetonitrile–water mixture (55 to 100%) at the slow rate 1.0 mL/min, column temperature 40°C, and aliquot volume 10 μL. The optimal excitation and emission wavelengths were determined using LC Solution software. Standard solutions of PAHs and their mixtures (Supelco and Dr. Ehrenstorfer GmbH) were used as references. The peak area was used as the analytical signal. Degree of PAH extraction (the "introduced-found" method) was 80 to 90%, no matrix effects were observed. The procedure allowed the detection with accuracy 25%, at confidence level 0.95.

RESULTS AND DISCUSSION

Air pollution with PAH is determined by the level and composition of anthropogenic emission as well as landscape and meteorology conditions.

The following HMPAHs were identified and quantified in air samples collected in the cities hosting WC-2018 (in the order of the appearance in the chromatograms): benz(a)anthracene (BaA), chrysene (CHR), benz(e) pyrene (BeP), benz(b)fluoranthene (BbF), benz(k) fluoranthene (BkF), benz(a)pyrene (BaP), dibenz(a,h) anthracene (DBahA), benz(g,h,i)perylene (BPL), and inden[1,2,3-*c*,*d*]pyrene (INP). The total PAH concentra-

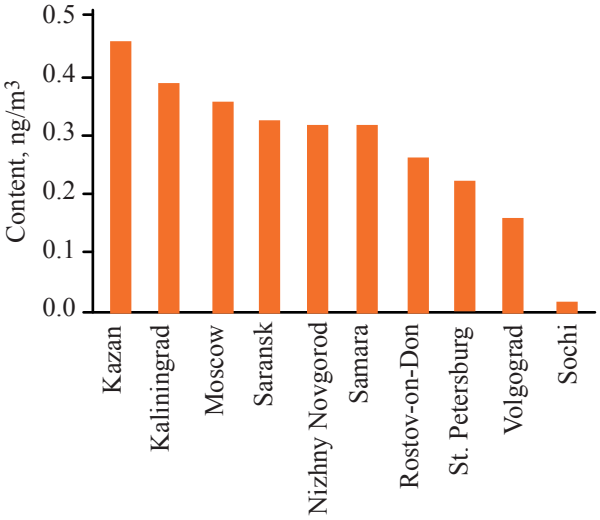

Fig. 2. Average content of benz(a)pyrene in the air of the cities hosting FIFA World Cup 2018.

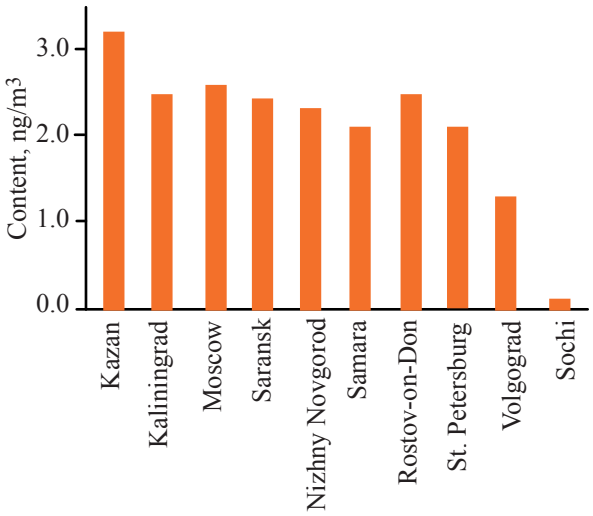

Fig. 3. Average content of HMPAH in the air of the cities hosting FIFA World Cup 2018.

tion was determined as a sum of 9 polyarenes (4 to 6 fused rings).

The data on the lowest and highest concentration of HMPAHs in June-July 2018 as well as their average monthly concentration are collected in Tables 2 and 3.

The air pollution was evaluated by comparing the actual benz(a)pyrene concentration with it MPC (1 ng/m^3). The content of other HMPAH is not subject to national regulation.

The high or extremely high air pollution with benz(a) pyrene was not observed in the cities hosting WC-2018. The highest benz(a)pyrene concentration (0.83 ng/m^3) and total HMPAH content (9.61 ng/m^3) during the observation period were observed in Kazan (station no. 8, Vakhitovskii district, July). The average concentration of benz(a)pyrene during two summer months did not exceed the MPC (Table 4). The obtained data revealed that the content of PAHs at the considered observation stations was low and comparable to that during previous years (Table 4). It should be noted that the average BaP concentration was about twice higher in the urban air in Moscow and St. Petersburg during WC-2018, likely due to the enhanced traffic.

Average concentration of benz(a)pyrene in the air was between 0.45 ng/m^3 in Kazan and 0.01 ng/m^3 in Sochi (Fig. 2). The air pollution in the hosting cities during WC-2018 was considered low. The same trend in the pollutant concentration depending on the sampling city was observed for other HMPAHs (Fig. 3).

The lowest concentrations of benz(a)pyrene (0.007 ng/m^3) and total HMPAH (0.09 ng/m^3) were observed in Sochi (station no. 4, June). The low concentrations of the pollutants at Sochi were likely due to the lower volume of the consumed fuels, more favorable conditions of spreading and eliminations of the pollutants, and accelerated photochemical processes of PAH transformation in the reactions with gaseous components.

Analysis of the features of the average concentrations of PAH in the air of the cities hosting WC-2018 (Table 3, Figs. 2–3) revealed that they were comparable, except for the case of Sochi.

The fraction of BaP in the total HMPAH content in the air ranged between 6.6% (St. Petersburg) and 10.5% (Kaliningrad). The correlation coefficient between the concentration of benz(a)pyrene and the total HMPAH content was above 0.9.

Analysis of the PAHs origin is a complicated affair. In general, it is reduced to the identification of the pyrogenic or petrogenic pollution sources using the molar ratio of PAHs [10, 16–19]. The sources of HMPAH in the air of the cities hosting WC-2018 were elucidated from the profiles of the content of polyarenes and the BaA/(BaA+CHR), BaP/(BaP+CHR), and INP/ (INP+BPL) molar ratios.

The average BaA/(BaA+CHR) ratio in the sampled air ranged between 0.41 (Sochi) and 0.63 (Rostov-on-Don), that of BaP/(BaP+CHR) was 0.25 (Volgograd) to 0.40 (Rostov-on-Don), and that of INP/(INP+BPL) was

Table 3. Average content of HMPAH in the air of the cities hosting FIFA World Cup 2018, ng/m³

City, month, and number of monitoring stations		BaA	CHR	BeP	BbF	BkF	BaP	DBahA	BPL	INP	Total HMPAH
Moscow	June, $n = 6$	0.57	0.51	0.31	0.15	0.19	0.25	0.01	0.35	0.31	2.56
	July, $n = 7$	0.95	0.92	0.91	0.30	0.40	0.44	0.03	0.76	0.51	5.23
Sochi	June, $n = 1$	0.02	0.02	0.01	0.005	0.005	0.007	< 0.001	0.01	0.01	0.09
	July, $n = 1$	0.01	0.02	0.02	0.02	0.007	0.013	< 0.001	0.03	0.02	0.14
Kaliningrad	June, $n = 3$	0.52	0.44	0.29	0.29	0.20	0.28	0.02	0.39	0.38	2.80
	July, $n = 3$	0.72	0.74	0.43	0.38	0.40	0.49	0.02	0.63	0.60	4.42
Nizhny Novgorod	June, $n = 3$	0.78	0.74	0.53	0.23	0.28	0.38	0.02	0.55	0.46	3.98
	July, $n = 2$	0.66	0.55	0.59	0.11	0.28	0.20	0.01	0.34	0.25	2.99
St. Petersburg	June, $n = 8$	0.44	0.35	0.62	0.44	0.29	0.12	0.007	0.18	0.07	2.52
	July, $n = 6$	0.97	0.92	0.84	0.15	0.35	0.35	0.01	0.43	0.37	4.40
Kazan	June, $n = 5$	0.59	0.54	0.36	0.26	0.39	0.42	0.02	0.61	0.47	3.66
	July, $n = 5$	0.87	1.04	0.78	0.42	0.59	0.49	0.02	0.81	0.61	5.64
Saransk	June, $n = 2$	0.42	0.45	0.35	0.12	0.15	0.23	0.01	0.31	0.26	2.31
	July, $n = 2$	0.77	1.02	1.1	0.19	0.32	0.41	0.03	0.62	0.48	4.92
Rostov-on-Don	June, $n = 3$	0.98	1.02	0.64	0.50	0.37	0.33	0.03	0.70	0.66	5.22
	July, $n = 3$	0.47	0.14	0.46	0.16	0.16	0.18	0.008	0.34	0.23	2.16
Volgograd	June, $n = 3$	0.43	0.46	0.33	0.17	0.19	0.22	0.01	0.41	0.32	2.54
	July, $n = 2$	0.20	0.28	0.53	0.03	0.06	0.06	0.007	0.10	0.07	1.32
Samara	June, $n = 3$	0.41	0.24	0.23	0.12	0.12	0.16	0.01	0.23	0.20	1.71

Table 4. Average concentration of benz(a)pyrene in the air hosting FIFA World Cup 2018 during June and July in 2016–2018, ng/m³

City and number of monitoring stations	Average concentration (concentration range), ng/m³		
	2016	2017	2018
Moscow, $n = 14$	0.14 (0.10.–0.30)	0.18 (0.01–0.40)	0.35 (0.11–0.68)
Sochi, $n = 2$	0.008 (0.006–0.010)	0.01 (0.006–0.015)	0.01 (0.007–0.013)
Kaliningrad, $n = 6$	0.25 (0.10–0.30)	0.11 (0.04–0.19)	0.38 (0.23–0.54)
Nizhny Novgorod, $n = 6$	0.51 (0.30–1.10)	0.13 (0.10–0.16)	0.31 (0.19–0.42)
St. Petersburg, $n = 14$	0.10 (0.02–0.20)	0.12 (0.03–0.30)	0.22 (0.03–0.57)
Kazan, $n = 10$	0.34 (0.04–0.80)	0.26 (0.07–1.10)	0.45 (0.19–0.83)
Saransk, $n = 4$	0.37 (0.20–0.50)	0.28 (0.17–0.35)	0.32 (0.19–0.60)
Rostov-on-Don, $n = 6$	0.32 (0.20–0.50)	0.26 (0.12–0.38)	0.26 (0.13–0.46)
Volgograd, $n = 6$	0.38 (0.19–0.51)	0.03 (0.01–0.06)	0.16 (0.03–0.24)
Samara, $n = 6$	0.25 (0.10–0.30)	0.22 (0.08–0.54)	0.31 (0.10–0.53)

0.36 (St. Petersburg) to 0.49 (Kaliningrad). The obtained data evidenced the pyrogenic nature of the HMPAH in the urban air, the main source of its pollution in summer likely being motor transport.

CONCLUSIONS

(a) 71 average monthly probes of air were sampled at 39 monitoring stations in 10 cities of the European part of Russia in June and July 2018, and the contents of 9 HMPAH were determined by means of HPLC.

(b) The average monthly concentration of benz(a) pyrene in the air samples in June and July 2018 did not exceed the MPC in the cities hosting WC-2018. The highest monthly concentration of benz(a)pyrene was observed at Kazan (station no. 8, June, 0.83 ng/m^3) and in Moscow (station no. 20, June, 0.68 ng/m^3).

(c) The average concentration of benz(a)pyrene in air of the considered cities decreased along the series: Kazan (0.45 ng/m^3), Kaliningrad (0.38 ng/m^3), Moscow (0.35 ng/m^3), Saransk (0.32 ng/m^3), Nizhny Novgorod (0.31 ng/m^3), Samara (0.31 ng/m^3), Rostov-on-Don (0.26 ng/m^3), St. Petersburg (0.22 ng/m^3), Volgograd (0.16 ng/m^3), Sochi (0.01 ng/m^3). The concentrations of other HMPAHs followed approximately the same trend.

(d) The air pollution with benz(a)pyrene in the cities hosting WC-2018 was considered low.

(e) Analysis of the relative content of PAHs in the urban air during WC-2018 evidenced the pyrogenic nature of the pollution. Likely, its main source was the motor vehicles, typical of large cities in summer.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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