

POSSIBILITY OF MONITORING OF PAHs DISTRIBUTION IN THE VERTICAL PROFILE AT THE BACKGROUND METEOROLOGICAL STATION KŘEŠÍN

GABRIELA STRNADOVÁ^{a,b,*}, VLASTIMIL HANUŠ^c, DAVID KAHOUN^b,
PETR SEMERÁK^a, JAN TRÍSKA^{b,c}

^a Czech Technical University in Prague, Department of Physics, Faculty of Civil Engineering, Thákurova 7, 166 29 Praha 6 – Dejvice, Czech Republic

^b University of South Bohemia in České Budějovice, Institute of Chemistry and Biochemistry, Faculty of Science, Branišovská 1760, 37005 České Budějovice, Czech Republic

^c Global Change Research Institute, v.v.i., Czech Academy of Sciences, Bělidla 4a, 603 00 Brno, Czech Republic

* corresponding author: gstrnadova@prf.jcu.cz

ABSTRACT. The contaminants present in the atmosphere have a substantial impact on public health. Among contaminants, the most important are polycyclic aromatic hydrocarbons (PAHs).

This paper is focused on the possibility of continuous PAHs monitoring and the description of their vertical distribution using filters, which serve to purify the air before the determination of the greenhouse gases (CO₂, CH₄, N₂O, CO, ozone) and Hg in air, continuously sampled at 8, 50 and 230 m at the atmospheric station Křešín near Pacov and elaboration of a simple and economical method of extraction of these filters.

The station serves as a point for monitoring the occurrence and remote transport of greenhouse gases and selected atmospheric pollutants and for the measurements of basic meteorological characteristics.

In December, 17, 2014, a sampling of 16 priority PAHs started and lasted until December, 9, 2015. Samples were taken approximately once a month. The maximum concentration of ΣPAHs was 15.905 ng/m³, measured at the height of 8 meters in the period of 11. 2. 2015–11. 3. 2015, the concentration of benzo[a]pyrene exceeded the emission limit in this period by more than 50%.

By the sampling, the hypothesis about decreasing concentration of PAHs with increasing height was confirmed, especially the decrease of heavier PAHs.

The sampling has shown that it is highly desirable to use the meteorological tower for sampling of PAHs using PTFE filters either by including the active sampler itself, or by using pre-filters for tropospheric ozone and gaseous elemental mercury analysers.

KEYWORDS: vertical profile; polycyclic aromatic hydrocarbons (PAHs); air quality; extraction procedure; HPLC; Meteorological station Křešín.

1. INTRODUCTION

Air pollution is a current problem that causes not only climate change, but also global major health problems. International community and large number of states over the world try to regulate the production, use and release of pollutants while providing as much information as possible on the health risks associated with these substances.

Among the substances that are severely damaging the environment and human society is a group of substances called polycyclic aromatic hydrocarbons (PAHs). The occurrence of these substances is typical in both the environment and in the food chain. The group of these substances is characterized as persistent for the environment, carcinogenic and endangering healthy foetal development [19]. It is a large group of substances, occurring mainly in complex mixtures, whose molecules consist of two or more condensed rings. The representative of these

compounds, benzo[a]pyrene, is a confirmed carcinogen [19, 45]. PAHs are substances of a lipophilic nature, abundantly distributed into the body, usually bound in fat tissues (liver, kidney) and smaller amounts in the adrenal glands, spleen and ovaries, where they accumulate. Signs and symptoms of toxic effects may occur many years after the exposure, or in subsequent generations. PAHs enter the body not only through the breathing patches, but also through the skin and gastrointestinal tract [25, 36].

A number of studies regarding urban pollution and its connection to the traffic load has been published [2, 5, 7, 12, 20–23, 30, 39]. Atmospheric pollution was also measured indirectly by moss bags or soil [4, 38] and it indicates a greater incidence of PAHs in an urban air, typically concentrated near urban centres and their concentrations correlate with transport or with combustion of fuels. Lower concentrations are found in outdoor air in remote areas [9] or due to long

distance transport [1, 10, 11]. Unfortunately, high concentrations of PAHs were also detected in residential buildings, e.g., in dormitories and offices [13, 15].

The main problem of the contamination of the environment by PAHs is their mobility, which varies by molecular weight. Higher molecular weight PAHs are relatively immobile due to their high molecular weight and their extremely low volatility and solubility. Therefore, they are primarily adsorbed onto dust particles, which then fall with the precipitation into the soil and water. More mobile PAHs include many compounds that differ in the number and position of the aromatic rings and the position and type of substituents. Such PAHs can be found in remote locations of the Earth far from their origin [34, 45]. Sorption of PAHs occurs on solid particulate matter (SPM) (dust, ash, soot, etc.) or aerosol droplets [19]. The retention in the atmosphere is, of course, dependent on the "favourable" climatic conditions. On the SPM surface, the PAHs are subjected to chemical reactions, they react with other pollutants, such as ozone, nitrogen oxides and sulphur dioxide to form oxygen containing compounds (hydroxy and keto PAHs), nitro- and dinitro-PAHs or sulfonic acids. In the air, PAHs are exposed to photooxidation, due to the presence of ozone, OH radicals and NOx.

Environmental monitoring has become an important indicator of pollution by individual harmful substances and assessing the quality of life as a whole. This information can then be linked to regulatory and national legislation.

1.1. LEGISLATION DATA SOURCES

According to the valid legislation of the Czech Republic is obliged to monitor the state of the air throughout the whole state territory, to monitor emissions and to regulate the discharge of pollutants into the air. Immission limits are set out in the Act on Air Protection [40, as amended] and in the Decree on the Method of Assessment and Evaluation of Pollution Level, the scope of information on the public about the level of pollution in smog situations [41, as amended]. For benzo[a]pyrene, this value is shown in Table 1.

This activity serves not only as legislative instruments for the control of individual polluters, but also as a built up network of monitoring stations operated by the Czech Hydrometeorological Institute together with private entities [31, 43].

The US-EPA and IARC selected the entire group of 16 major polycyclic aromatic hydrocarbons for the targeted and long-term monitoring, namely (chemical name and acronym): naphthalene (NA), acenaphthylene (ACL), acenaphthene (ACN), fluorene (FL), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLU), pyrene (PY), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), benzo[ghi]perylene (BghiP) and dibenzo[a,h]anthracene (DBahA).

Pollutant	Averaging time	Immission limit (ng/m ³)
Benzo[a]pyrene	Calendar year	1

TABLE 1. Immission limit for health protection — total content in PM₁₀ particles.

1.2. MONITORING OF PAHs IN VERTICAL PROFILE

Monitoring of these 16 PAHs in the unrestricted air is the topic of many publications, but not very often the vertical concentration profile of PAHs was studied. The following studies are dealing with measurements on the roofs of buildings, garages and also in various floors of residential buildings on busy roads (rooftop on expressway, highway, locksides, warehouse, industrial harbour, and central Nagoya [9]; a building in an urban area [6]; a building in an urban area and heavy traffic [24]; a building in an express highway area [18]; industry and residential rooftops [14]; a building in an urban area [4]; a building in an urban area [37]. The overview of the main literature sources regarding measurements of PAHs and their vertical distribution is given in Table 2.

Some publications deal with the determination of the vertical profile of PAHs in urban or industrial agglomerations [28, 35, 39]. Studies of the authors focused on the vertical monitoring of PAHs at higher heights in the countryside are rather limited, e.g., roof buildings at 3 m height in the farms, farm area [3], a campus area close lake — 2.5 m [33]; a rural area at 4 m height [26].

A few publications are dedicated to the determining of the PAHs vertical profile at a different heights of the above mentioned towers: an urban area of Toronto city, CN tower [8]; the urban tower [35, 39]; the scaffolding tower in the forest canopy [16]; the Milad Tower of Tehran, urban area [28].

The authors did not find any publication that would deal with the vertical profile of PAHs at the background station and simultaneously measured PAHs during the sampling time continuing for one month.

1.3. AIR MONITORING ON THE EUROPEAN CONTINENT — OBSERVATORIES

Air monitoring in Europe was backed up with a unique program of the ACTRIS (Aerosol, Clouds, and Trace gases Research InfraStructure Network), which offers a comprehensive program of measurements of a vertical distribution of the aerosol, its properties and amounts of trace gases. These observations have, at some stations, a long history. From 18 observation stations, 16 stations are deployed in Europe, one station is in Madagascar and one in Tenerife. Only 4 stations (Italy, southern Sweden, Cyprus and the Czech Republic) are dedicated to the monitoring of dust particles PM₁, PM_{2.5} and PM₁₀. The Finnish station is dedicated, as the only one, to dealing with continual determination

Article	City/Country	Season	Note	3–4 m	8–16 m	20–32 m	36–44 m	60–65 m	100–158 m	200–240 m	300–330 m
[39]; 16 PAHs	Tianjin/China	Dec/Jan	urban, tower			265/409	333/537	239/359			
[35]; 16 PAHs	Peking/China	Jan/Mar	urban, tower		440.9/48.8	* /45.5	414.6/*	396.6/52.7	460.1/21.2	174.0/30.7	62.2/29.0
[29]; 23 PAHs	Nagoya/Japan	average	express highway for four dockside warehouse seasons, central Nagoya industrial harbour, urban residential			2.3–30.1 1.1–22.4 1.0–14.7 1.6–22.1 3.1–17.5					
[6]; 13 PAHs	Liwan/China	Nov–Dec	urban, building			32.5–153.7					
	Wushan/China	Oct–Nov	urban, building			70.8–93.6					
	Xingken/China	Oct	suburban, field	39.2							
[33]	Campo Grande /Brazil	Jul–Nov	campus close to lake	58.9–62.5							
[26]; 23 PAHs	North central part/India	winter /summer /rainy	rural	58.2/175.4 52.4							
[24]; 18 PAHs	Guangzhou/China	Nov	urban, heavy traffic, building	83		40.8					
[18]	Singapore		express highway, building		5.7–6.8	4.5–6.7	0.1–4.7				
[16]	Southern Ontario /Canada	spring	forest, scaffolding tower (1.5m)	0.2–0.4	1–0.5	0.1–0.6	0.1–0.4				
[28]	Tehran/Iran	year	urban, Milad Tower		16.2	19.4	12.8	14.2			
[32]	Bangkok/Thailand	Feb	urban, building			0		0.5			0.2
[37]	Mumbai/India	winter	urban, building	39.0–42.0	21.0–25.0						
[14]	Xiamen/China	summer /autumn	industry, rooftop residential, rooftop		5.2/37.0 1.7/26.6						
[3]	mid part/Korea	Feb/May	urban	109/22.9							
			urban	410/105							
			rooftop, rural, farm	119/74.1							
			rooftop, rural, farm	195/91.8							

TABLE 2. The overview of the literature sources regarding measurements of PAHs and their vertical distribution. Unit expressed in ng/m^3 for Σ PAHs, the star * signifies the sampling was failed.

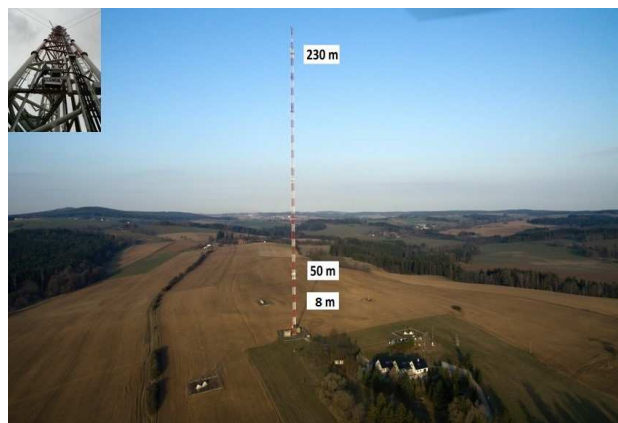


FIGURE 1. Czech National Monitoring Point Křešín — a steel tower of 240 metres height.

of PAHs from the atmosphere [44]. Tropospheric ozone is measured at 5 stations (Italy, France, Finland, Czech Republic and Spain) and gaseous elemental mercury is measured only in Finland and in the Czech Republic.

1.4. THE GOAL OF THE STUDY

The goal of the study was the evaluation and verification of the possibility of monitoring of PAHs distribution from the pre-filters of mercury and ozone analysers available on Křešín meteorological tower and the elaboration of a simple and economical method of an extraction of these filters.

This study also focused on a proposal of filter replacement periods, suggestion of sampling heights and filter porosity to obtain high-quality data so that a continual long-term monitoring of the vertical distribution of pollutants in the atmosphere could be continued in the following years.

2. MATERIALS AND METHODS

2.1. MATERIALS

This study was conducted in the neighbourhood of Košetice Observatory (N 50°35', E 15°05', elevation 534 m). Very close to the existing meteorological observatory in Košetice, the high atmospheric tower (height 240 meters) for scientific purposes was built in 2012 on the locality Křešín, fulfilling the function of the Czech National Monitoring Point for the monitoring and long-term measurements of the greenhouse gases content in the air and monitoring of the air cleanliness in higher atmospheric layers.

As can be seen in the picture (Figure 1), the site is located in a relatively flat landscape. The tower is owned by the Global Change Research Institute, v.v.i., Czech Academy of Sciences. The operator goes to the top by the rack electric elevator through the centre of the tower. The tower is anchored by five steel ropes and three giant reinforced concrete basis. [42, 43].

On the tower, there is, among other items, continuous determination of ozone and mercury. Prior to these analysers, 47 mm PTFE filters, 5 µm porosity



FIGURE 2. Placement of PTFE filter in continuous analyser of tropospheric ozone.

for the ozone analyser and 0.2 µm for mercury analyser, both located in the PTFE holder (Figure 2) were placed in the line in order to prevent particulate matter from penetrating the analysers. In front of these filters is a polyamide net against insects and coarse particulate matter. The air is not subjected to drying.

2.2. METHODS

After collection, the filters were packed in an aluminium foil and then sealed to a plastic foil and dispatched to the laboratory for the analysis. If the filters were not immediately analysed, they were stored in the freezer at -18°C . It was found experimentally that this temperature is sufficient to avoid a degradation of the PAH.

All laboratory glassware was washed three times with redistilled water, then 3 times with a 1 : 1, (v/v) solvent mixture of acetone : hexane and dried at a room temperature. After the use, the glassware was washed again, first, the tap water was used, followed by a distilled water, followed by a redistilled water and a solvent mixture as described above. When determining the reproducibility, the glass was washed immediately after use. The laboratory glass was stored in the locked cabinet in reverse, or the throat was covered with an aluminium foil.

Samples of filters were always analysed in series, in order to comply with the same extraction conditions. In the laboratory, the collecting filter was carefully removed with tweezers from the aluminium foil and inserted into an Erlenmeyer flask, to which 10 ml of a mixture of extraction agents was added, which was formed by acetone : hexane (1 : 1, v/v). Each sample was spiked with 100 µl of 9,10-diphenylanthracene (as an internal standard) with the concentration of 100 µg/l. The sample was placed in an ultrasonic bath and extracted for 10 minutes. After this time, the extraction solvent was transferred into the pear shaped flasks. The extraction was repeated with 10 ml of the extraction reagent for 10 minutes and this second part was adding too. Then, 500 µl of keeper (a mixture of isopropanol : diethylene glycol in a ratio

Sampling points			
Date of collection	8 m	50 m	230 m
14. 1. 2015	6.683	4.859	4.125
11. 3. 2015	15.905	11.867	9.624
8. 4. 2015	5.372	3.881	3.369
6. 5. 2015	1.533	1.033	0.741
27. 5. 2015	0.894	0.609	0.449
17. 6. 2015	0.415	0.34	0.368
15. 7. 2015	0.238	0.179	0.208
9. 9. 2015	0.458	0.399	0.416
7. 10. 2015	1.555	1.2	0.821
11. 11. 2015	4.223	2.68	0.654
9. 12. 2015	5.231	3.72	1.94

TABLE 3. The sum of PAHs at different height trapped on the filters in front of the ozone analyser (ng/m³)

Sampling points	
Date of collection	Ground
3. 12. 2014	7.367
17. 3. 2015	8.022
8. 4. 2015	5.702
6. 5. 2015	2.222
3. 6. 2015	0.799
1. 7. 2015	0.347
29. 7. 2015	0.366
9. 9. 2015	0.463
7. 10. 2015	1.882
31. 10. 2015	4.03
2. 12. 2015	4.111

TABLE 4. The sum of PAHs at ground trapped on the filters in front of the mercury analyser (ng/m³).

of 4 : 1, v/v) was added and the extract evaporated in a rotary vacuum evaporator nearly to dryness. The rest of the keeper, containing the analytes, in the pear shaped flask was diluted with 1 ml of mobile phase (acetonitrile : double-distilled water in a ratio of 1 : 1 v/v) and transferred into an Eppendorf vial. The sample was cleaned and cleared of solid impurities by centrifugation at 15000 rpm, 20 °C for 10 minutes. The supernatant (approximately 800 µl) was carefully removed by a syringe from the centrifuge tubes and transferred into a dark vial for analysis.

Analysis of the extracts was performed according to the described method (Supelco Application no. 118) with a small modification by HPLC-DAD-FLD, both detectors connected in series. The following reagents were used for the sample preparation and for the analysis. Acetone (for organic Ultra Resi-analyzed), J.T.Baker, hexane (for organic Ultra Resi-analyzed), J.T.Baker, isopropyl alcohol (suitable for liquid Chromatography and UV-Spectrophotometry, Chrom AR HPLC), Macron, acetonitrile (Chrom AR HPLC Super Gradient), Macron, diethylene glycol (puriss p.a.), Sigma-Aldrich and PAH-mix, Dr. Ehrenstorfer GmbH (X 20950009A, lot: 30325AL) 100 ng/µl in acetonitrile. Gradient elution was used in the analysis.

This method had the following conditions: a Dionex Ultimate liquid chromatograph from Thermo Scientific (USA) was used for the analysis, two detectors were used in series, the DAD 3000 RS spectrophotometer for acenaphthylene analysis and the fluorescence detector FLD 3000 RS to determine the other 15 PAHs. The chromatographic column was a Waters PAH C18 column (250 × 3 mm; 5 µm), eluting with a gradient. Eluent A: water/acetonitrile 1 : 1 (v/v), eluent B: 100 % acetonitrile, mobile phase: flow rate: 1 ml/min, column temperature: 35 °C and 90 µl sample injection. This method was performed with a very good separation and validation of the measured results.

The calibration curve was routinely analysed and validated in the range of 0.1–10 µg/l (7 concentration levels, each in 3 independent repeats).

3. RESULTS AND DISCUSSION

For the determination of PAHs, there are many methods for qualitative and quantitative analysis and many techniques for pre-cleaning of the samples from individual matrices in the literature. The question of which method to choose is probably the most important one. The vast majority of publications propose the extraction procedure using the Soxhlet extraction [3, 16, 28, 32, 35], alternatively, an extraction in the ultrasonic bath [24, 27, 30, 31, 33]. As extraction agents, a variety of solvents, mainly dichloromethane, methanol, petroleum ether and others, was used.

The chromatographic analysis of the PAHs was largely based on GC/MS [3, 6, 16, 18, 24, 28], GC/MS-MS [32] and GC/LRMS [27]. As an example of liquid chromatography application for the analysis of PAHs is the publication [31]. For the analysis of 10 heavier PAHs, they used FLD detector, column Pursuit 3 PAH (100 × 4.6 mm), mobile phase acetonitrile : water (60 : 40) and flow rate 0.5 ml/min.

Our work was focused on the monitoring of the PAHs at the Křešín background station and their analysis in December 2014–December 2015 in the vertical profile, while 16 US EPA PAHs were analysed in the monthly sampling interval. We have chosen the ultrasonic extraction using acetone : hexane (1 : 1, v/v) as the extraction solvent and the liquid chromatography using FLD detector for the analysis.

The values presented in the following tables are the sum of the PAHs for individual periods found on dust particles on filters with a porosity of 5 µm and 0.2 µm, which means that a fractions of 5 µm particles and greater were trapped on the filters of the ozone analyser (Table 3) at different heights and fractions of 0.2 µm and higher were trapped on the filters of the mercury analyser (Table 4) on the ground.

The total concentration of the PAHs adsorbed on dust particles and trapped on filters from the ozone analyser in the period of 11. 2. 2015–11. 3. 2015 shows the highest concentration at all three heights (8, 50



FIGURE 3. Concentration of individual PAHs (16 PAHs according U.S. EPA) at different heights trapped on the filters from ozone analyser. Sampling period 17. 12. 2014–12. 2015. Unit expressed in ng/m^3

and 230 m) 15.905, 11.867 and $9.624 \text{ ng}/\text{m}^3$ with a decreasing concentration trend with a higher sampling height. The lowest total concentration of the PAHs of $0.179 \text{ ng}/\text{m}^3$ is then found at the height of 230 m from the period of 17. 6. 2015–17. 7. 2015, with a value of $0.208 \text{ ng}/\text{m}^3$ from 230 m height and value of $0.238 \text{ ng}/\text{m}^3$ at height of 8 m.

When we compare the concentration levels from different heights, we can see a trend of a decreasing concentration of the PAHs with increasing height: concentration measured at different levels from 8 to 320 m on the tower [35], 4 and 20 m [37]; 24 and 36 m [24]; for comparison, see Table 2. Steeply decreasing tendency with height in 30, 90, 150, 210, 270 and 360 meters on the Toronto CN Tower is also reported [8], where it points out urban areas as the source of pollution. In the scientific study [39], the highest concentration is at 40 m height in the winter period (measured heights of 20, 40 and 60 m) in the urban area. The authors of [17] monitored gradient dependence of 8 PAHs concentration in different floors of buildings in New York, with the highest concentrations of nonvolatile and semivolatile PAHs found on the 3rd-5th floor compared to the monitored PAHs in 0-2nd and 6th–32nd floors. Pongpiachan [32] found the highest concentration in 158 m compared to 38 and 328 m in winter in the urban atmosphere of Bangkok City. A measurement on a scaffolding tower 45 m high in the leafy forest in Canada, where the sampling points were in 1.5, 16.7, 29.1 and 44.4 m, were performed [16] and

they noted a decrease in lower PAHs in the gas phase with the height, namely phenanthrene, anthracene, and pyrene.

In the context of decreasing concentration with height, several publications also mentioned the current drop in summer, as opposed to the winter season [3, 14, 26, 35]. The authors of [26] compared not only the winter and summer season, but also the rainy season, in which the PAHs concentrations were the lowest.

Most of these publications focus only on a short sampling time, because of a higher financial cost of active sampling.

Overview of the measurements for four individual seasons at 20 m height is reported [29], their sampling is limited for only 3 days, but for 4 seasons. The vertical profile during October 2011–March 2012 was monitored [28], however, the results are presented as the sum of individual PAHs for all periods, the contribution of 200 and 300 m concentration was explained as a long-distance transport of pollutants.

A uniform layering of PAHs in the atmosphere was supposed [35], but at the same time, the authors claim that this assumption is working with high uncertainties only and it is based on the estimation of atmospheric concentrations and their movement in the atmosphere.

Concentration of individual polycyclic aromatic hydrocarbons, starting from hydrocarbon with M.W. of $202 \text{ g}/\text{mol}$ (Fluoranthene), shows a trend of decreasing concentration with the height (Figure 3). The

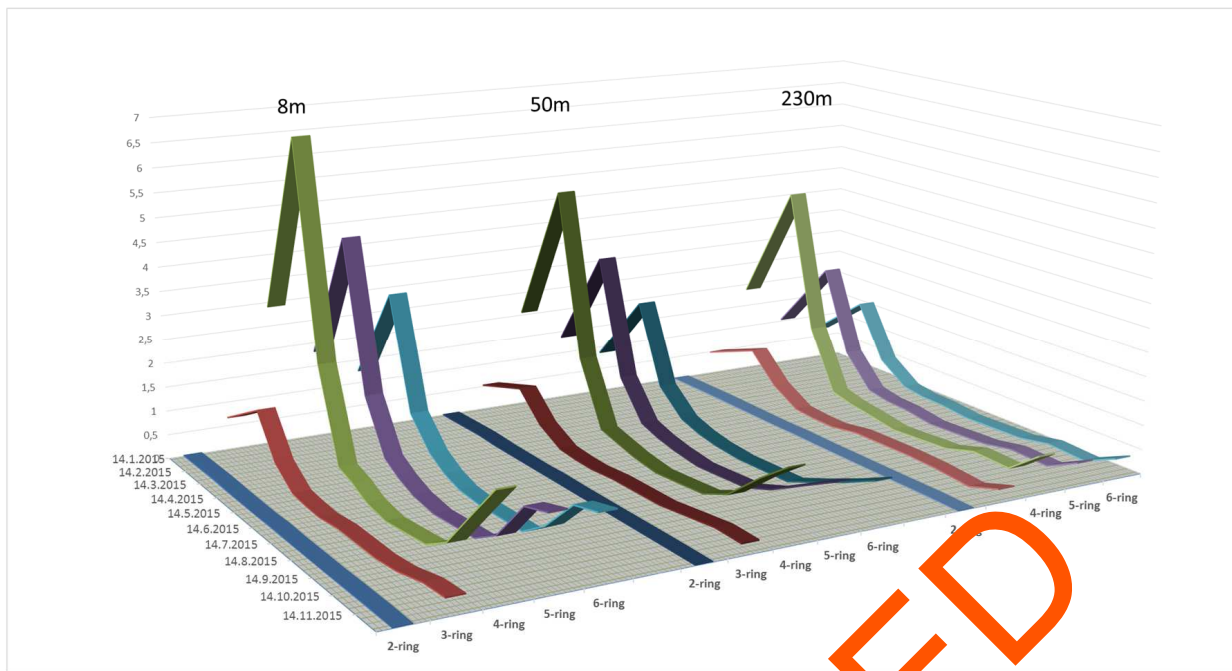


FIGURE 4. Concentrations of 2-, 3-, 4-, 5- and 6-ring PAHs measured on the tower at different heights, on the filters from ozone analysers: 2-ring PAHs include naphthalene; 3-ring PAHs include acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene; 4-ring PAHs include fluoranthene, pyrene, benzo[a]anthracene and chrysene; 5-ring PAHs include benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and benzo[ah]anthracene; 6-ring PAHs include indeno[123-cd]pyrene and benzo[ghi]perylene. Sampling period 17. 12. 2014–9. 12. 2015. Unit expressed in ng/m^3 .

PAHs with 4 to 6 aromatic rings have the highest concentration at all heights in the period of 11. 2. 2015–11. 3. 2015, with the concentration decreasing with increasing height and the lowest concentrations in the period of 17. 6. 2015–15. 7. 2015 at 230 m.

Figure 4 shows again the decrease in concentrations with height. Regarding the concentrations of lower molecular weight PAHs (2 and 3 rings), there is no such steep difference in concentration decrease in comparison with the higher molecular weight PAHs (the result may be distorted by acenaphthylene, whose concentration was below the detection limit during the year). The PAHs with 4 aromatic rings reached the highest concentrations in all periods at all measured heights.

In the Figure 3, it is possible to see that there is also a certain stable composition of PAHs throughout the sampling period, i.e., the meteorological station really measures the relatively stable background concentration of PAHs. In Figure 3, we can also see that PAHs create 4 dominant pairs of hydrocarbons. Their percent representation for a height of 230 m is shown in Figure 5.

The hypothesis that the proportion of heavier PAHs with the sampling height is decreasing was confirmed. This difference is minimal in the summer, which is related to the generally lower concentrations of all PAHs (the sum of PAHs was calculated starting from M.W. of 202 g/mol and higher) (Figure 6).

Table 5 from the ozone analyser represents the time

development of the concentration level of the individual PAHs, depending on the different sampling heights during the monitored period (the highest and lowest concentrations are marked with colour). It is clear from the Table 5 that the highest concentrations occurred at each sampling height in the period of 11. 2. 2015–11. 3. 2015, the maxima being at 8 m sampling height and the lowest concentrations occurred in the period of 17. 6. 2015–15. 7. 2015, with the lowest concentration being at 230 m sampling height.

During our research study, we also focused on benzo[a]pyrene (BaP), which is, according to the IARC, Group 1 carcinogen. This most carcinogenic and mutagenic hydrocarbon with 5 rings was found present in the air [3] in 2 places in an urban area with the concentration of 0.61 and 0.73 ng/m^3 in winter and in 2 places on a farm on the rooftop (3 m) with the concentration of 0.17 and 0.53 ng/m^3 in the same season. Nagoya metropolis was measured and authors [29] found the concentration of BaP inside and in peripheral area 0.06–1.45 ng/m^3 and 0.05–3.75 ng/m^3 , both in 20 m above the ground.

The large difference in the BaP concentrations in the winter and summer season is described in the article [33]. The authors measured the BaP at the height of 2.5 m in campus near Brazilian city Campo Grande and the concentration of the BaP was ranging from 8.9–62.5 ng/m^3 .

In spite of the fact that meteorological station Křešín near Pacov is a background station, the mea-

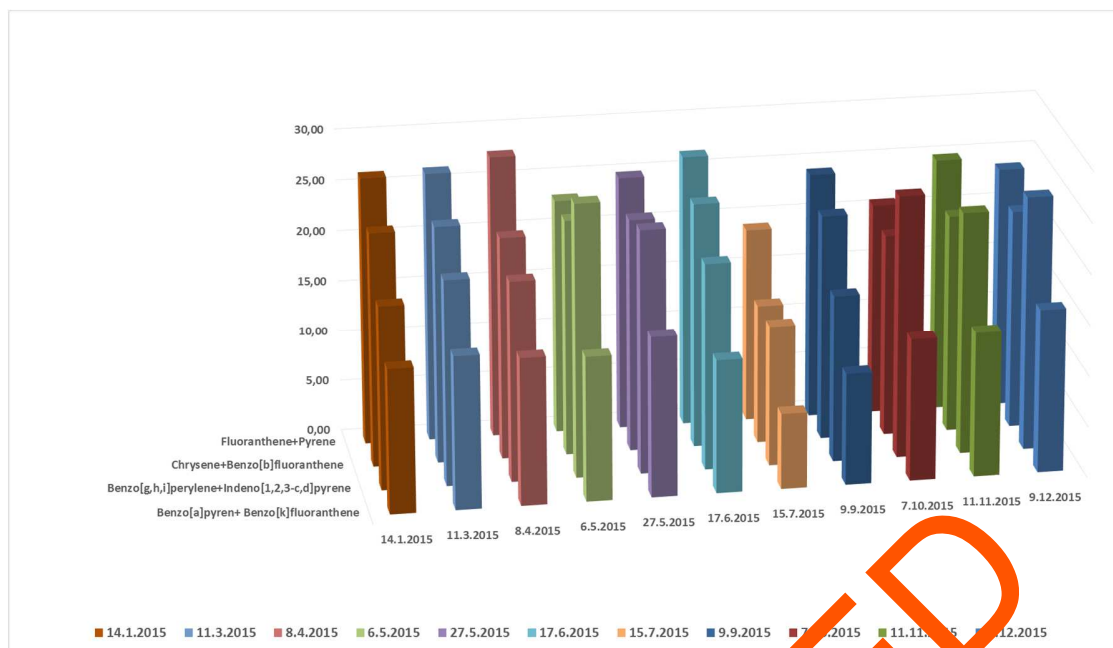


FIGURE 5. An example of the layering of four individual pairs in % at a height of 50m. Sampling period 17. 12. 2014–9. 12. 2015.

sured concentration of the BaP exceeded the limit value (see Table 1) in two cases (Figure 7), however, the proportion of heavier PAHs was significantly higher than the BaP. The highest concentrations of BaP we have measured were in the winter season (1.51 ng/m^3 for 8 m height) and 1.11 ng/m^3 for 50 m height and for the same period. In 230 m height, the BaP concentration of 0.85 ng/m^3 was under the immission limit.

3.1. FILTERS FROM MERCURY ANALYSER

As supplementary measurements, we present the values of the concentrations in the collection filters from mercury analyser at the base of the tower. The samples were taken at the sampling period different than in the case of the cone and dryer filters and filters also had a different porosity of $0.2 \mu\text{m}$, so these values cannot be compared adequately, however, again, higher concentrations of the PAHs in the winter months than in the summer months are clearly visible (Fig 8).

3.2. CONCLUSION

Measurements of PAHs concentrations from December 17, 2014 to December 9, 2015 at Křešín near Pacov meteorological background station have produced unique results. Unique, because in the literature, a continuous monthly sampling at different heights at the background station has not been described yet. The concentration of the PAHs measured at the Křešín near Pacov meteorological tower verified the hypothesis of the concentration decrease of the individual hydrocarbons with the increasing height and the dependence of this concentration on the season. The total concentration of the PAHs in this period was

15.005 , 11.867 and 9.624 ng/m^3 for heights of 8, 50 and 230 m.

The samples taken continuously for one month are characterizing the concentration of the individual PAHs observed during the year, especially the decrease in the concentration of high molecular weight PAHs along with increasing height. By the measurements, a higher proportion of heavier PAHs was found, for which no immission limits are set, e.g., concentration of the pairs of fluoranthene and pyrene in March 2015 (sum) 4.077 , 3.139 and 2.895 ng/m^3 , chrysene and benzo[b]fluoranthene 3.659 , 2.768 and 2.088 ng/m^3 , benzo[ghi]perylene and indeno[1,2,3-cd]pyrene 3.307 , 2.404 and 1.673 ng/m^3 compared to a pair of benzo[a]pyrene and benzo[k]fluoranthene 2.382 , 1.782 and 1.331 ng/m^3 at the height of 8, 50 and 230 m.

Higher concentrations of benzo[a]pyrene of 1.507 and 1.113 ng/m^3 , which exceeded the allowed immission limit value, were measured only in the winter of 2015 at two heights of 8 and 50 m, which could be caused by the heating season.

Due to the interesting results from 2015, the authors will continue to carry out further measurements not only on PTFE filters on already existing equipment, but also on passive analysers located directly on the meteorological tower (PUF and XAD sorbents). Another goal is to conduct a pilot single air sampling from one specific height (230 m) using the portable active SKC Leland Legacy sampler, which has its own filtration equipment (PTFE or Quartz filters). Measurement of PAHs will be complemented by weather data, such as wind direction, wind rotation, humidity, temperature and air pressure.

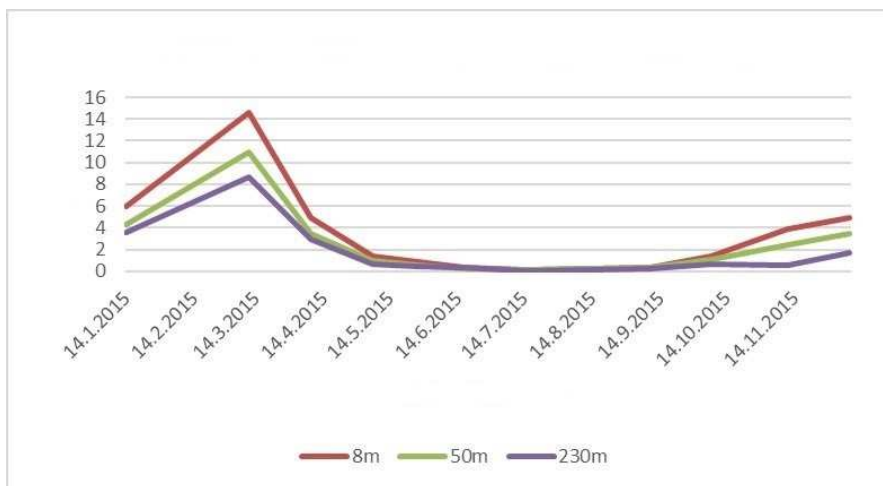


FIGURE 6. The sum of heavier PAHs concentration (4-6ring) for each height. The following PAHs are included: fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[g,h,i]perylene and dibenzo[a,h]anthracene, filters from ozone analysers. Unit expressed in ng/m^3



FIGURE 7. Concentration of benzo[a]pyrene in different periods and different heights, filters from ozone analysers. Unit expressed in ng/m^3

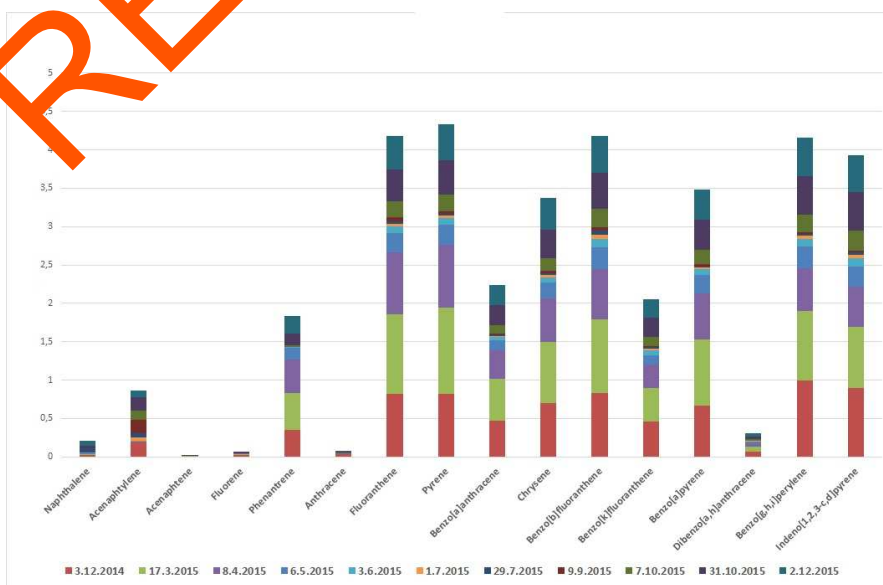


FIGURE 8. Sum of PAHs collection at the base of the tower, sampling period 31. 12. 2014–2. 12. 2015. Concentration of individual PAHs on the ground, filters from mercury analyser (ng/m^3)

ACKNOWLEDGEMENTS

The article was supported by the Czech Technical University grant SGS16/197/OHK1/3T/11 and by the Ministry of Education, Youth and Sports of CR within the National Sustainability Program I (NPU I), grant number LO1415 and the research was performed in the frame of the contract between Global Change Research Institute AS CR and Faculty of Natural Sciences, University of South Bohemia in České Budějovice. We also thank very much to colleagues from Global Change Research Institute AS CR for collecting filters in the tower of Křešín near Pacov, mainly Gabriela Vítková.

REFERENCES

- [1] AAMOT, Eli, Eiliv STEINNES a Rudolf SCHMID. Polycyclic aromatic hydrocarbons in Norwegian forest soils: Impact of long range atmospheric transport. *Environmental Pollution*. 1996, **92**(3), 275-280. doi:10.1016/0269-7491(95)00114-X
- [2] ANASTASOPOULOS, Angelos T., Amanda J. WHEELER, Deniz KARMAN a Ryan H. KULKA. Intraurban concentrations, spatial variability and correlation of ambient polycyclic aromatic hydrocarbons (PAH) and PM2.5. *Atmospheric Environment*. 2012, **59**, 272-283. doi:10.1016/j.atmosenv.2012.05.004
- [3] BAE, Soo Ya, Seung Muk YI a Yong Pyo KIM. Temporal and spatial variations of the particle size distribution of PAHs and their dry deposition fluxes in Korea. *Atmospheric Environment*. 2002, **36**(35), 5491-5500. doi:10.1016/S1352-2310(02)00666-0
- [4] CURTOSI, Antonio, Emilien PELLETIER, Cristian L. VODOPIVEZ a Walter P. MAC CORMACK. Polycyclic aromatic hydrocarbons in soil and surface marine sediment near Jubany Station (Antarctica). Role of permafrost as a low-permeability barrier. *Science of The Total Environment*. 2007, **383**(1-3), 193-204. doi:10.1016/j.scitotenv.2007.04.022
- [5] ČUPR, Pavel, Jana KLÁNKOVÁ, Tomáš BARTOŠ, Zuzana FLEGROVÁ, Jiří KŘEHOTEK a Ivan HOLOUBEK. Passive air sampler as a tool for long-term air pollution monitoring: Part 5. Air genotoxic potency screening assessment. *Environmental Pollution*. 2006, **144**(2), 406-411. doi:10.1016/j.envpol.2005.12.045
- [6] DUAN, Jingchun, Ximeng BI, Jihua TAN, Guoying SHENG a Jiamo FU. The differences of the size distribution of polycyclic aromatic hydrocarbons (PAHs) between urban and rural sites of Guangzhou, China. *Atmospheric Research*. 2005, **78**(3-4), 190-203. doi:10.1016/j.atmosres.2005.04.001
- [7] DUNBAR, Jana C, Chen-I LIN, Isaura VERGUCHT, Jeffery WONG a John L DURANT. Estimating the contributions of mobile sources of PAH to urban air using real-time PAH monitoring. *Science of The Total Environment*. 2001, **279**(1-3), 1-19. doi:10.1016/S0048-9697(01)00686-6
- [8] FARRAR, N. J., T. HARNER, M. SHOEIB, A. SWEETMAN a K. C. JONES. Field Deployment of Thin Film Passive Air Samplers for Persistent Organic Pollutants: A Study in the Urban Atmospheric Boundary Layer. *Environmental Science & Technology*. 2005, **39**(1), 42-48. doi:10.1021/es048907a
- [9] GOUIN, Todd, David WILKINSON, Stephen HUMMEL, Ben MEYER a Andrew CULLEY. Polycyclic aromatic hydrocarbons in air and snow from Fairbanks, Alaska. *Atmospheric Pollution Research*. 2010, **2010**(1), 9-15. doi:10.5094/APR.2010002
- [10] HALSALL, C.J., A.J. SWEETMAN, L.A. BARRIE a K.C. JONES. Modelling the behaviour of PAHs during atmospheric transport from the UK to the Arctic. *Atmospheric Environment*. 2001, **35**(2), 255-267. doi:10.1016/S1352-2310(00)00195-3
- [11] HALSALL, Crispin J., Peter J. COLEMAN, Brian J. DAVIS, Victoria. BURNETT, Keith S. WATERHOUSE, Peter. HARDING-JONES a Kevin C. JONES. Polycyclic Aromatic Hydrocarbons in U.K. Urban Air. *Environmental Science & Technology*. 1994, **28**(13), 2380-2386. doi:10.1021/es00062a024
- [12] HARNER, Tom, Michael PABTKOW, Ivan HOLOUBEK, et al. Passive air sampling for persistent organic pollutants: Introductory remarks to the special issue. *Environmental Pollution*. 2005, **144**(2), 361-364. doi:10.1016/j.envpol.2005.12.044
- [13] HASSANVALEDI, Mohammad Sadegh, Kazem NADDAFI, Sasan KARIDI, et al. Characterization of PAHs and metals in indoor/outdoor PM10/PM2.5/PM1 in a retirement home and a school dormitory. *Science of The Total Environment*. 2015, **527-528**, 100-110. doi:10.1016/j.scitotenv.2015.05.001
- [14] HONG, HuaSheng, HongLing YIN, XinHong WANG a JieXing YE. Seasonal variation of PM10-bound PAHs in the atmosphere of Xiamen, China. *Atmospheric Research*. 2007, **85**(3-4), 429-441. doi:10.1016/j.atmosres.2007.03.004
- [15] CHEN, Ying, Xinghua LI, Tianle ZHU, Yingjie HAN a Dong LV. PM 2.5-bound PAHs in three indoor and one outdoor air in Beijing: Concentration, source and health risk assessment. *Science of The Total Environment*. 2017, **586**, 255-264. doi:10.1016/j.scitotenv.2017.01.214
- [16] CHOI, S.-D., R. M. STAEBLER, H. LI, Y. SU, B. GEVAO, T. HARNER a F. WANIA. Depletion of gaseous polycyclic aromatic hydrocarbons by a forest canopy. *Atmospheric Chemistry and Physics*. 2008, **8**(14), 4105-4113. doi:10.5194/acp-8-4105-2008
- [17] JUNG, Kyung Hwa, Kerly BERNABE, Kathleen MOORS, Beizhan YAN, Steven N. CHILLRUD, Robin WHYATT a David CAMANN. Effects of Floor Level and Building Type on Residential Levels of Outdoor and Indoor Polycyclic Aromatic Hydrocarbons, Black Carbon, and Particulate Matter in New York City. *ATMOSPHERE*. 2011, **2**(2), 96-109. doi:10.3390/atmos2020096
- [18] KALAIARASAN, M., R. BALASUBRAMANIAN, K.W.D. CHEONG a K.W. THAM. Particulate-bound polycyclic aromatic hydrocarbons in naturally ventilated multi-storey residential buildings of Singapore: Vertical distribution and potential health risks. *Building and Environment*. 2009, **44**(2), 418-425. doi:10.1016/j.buildenv.2008.04.003
- [19] KIM, Ki-Hyun, Shamin Ara JAHAN, Ehsanul KABIR a Richard J.C. BROWN. A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. *Environment International*. 2013, **60**, 71-80. doi:10.1016/j.envint.2013.07.019

- [20] KLÁNOVÁ, Jana, Jiří KOHOUTEK, Lenka HAMPLOVÁ, Petra URBANOVÁ a Ivan HOLOUBEK. Passive air sampler as a tool for long-term air pollution monitoring: Part 1. Performance assessment for seasonal and spatial variations. *Environmental Pollution*. 2006, **144**(2), 393-405. doi:10.1016/j.envpol.2005.12.048
- [21] LEVY, JI, EA HOUSEMAN, JD SPENGLER, P LOH a L. RYAN. Fine particulate matter and polycyclic aromatic hydrocarbon concentration patterns in Roxbury, Massachusetts: a community-based GIS analysis. *Environ Health Perspect*. 2001, **109**(4), 341-7.
- [22] LEVY, JI., DH. BENNETT, SJ. MELLY a JD. SPENGLER. Influence of traffic patterns on particulate matter and polycyclic aromatic hydrocarbon concentrations in Roxbury, Massachusetts. *J Expo Anal Environ Epidemiol*. 2003, **13**(5), 364-71. doi:10.1038/sj.jea.7500289
- [23] LEVY, Jonathan I, Thomas DUMYAHN a John D SPENGLER. Particulate matter and polycyclic aromatic hydrocarbon concentrations in indoor and outdoor microenvironments in Boston, Massachusetts. *Journal of Exposure Analysis and Environmental Epidemiology*. 2002, **2002**(12), 104-114. doi:10.1038/sj/jea/7500203
- [24] LI, Chunlei, Jiamo FU, Guoying SHENG, Xinhui BI, Yongmei HAO, Xinming WANG a Bixian MAI. Vertical distribution of PAHs in the indoor and outdoor PM_{2.5} in Guangzhou, China. *Building and Environment*. 2005, **40**(3), 329-341. doi:10.1016/j.buildenv.2004.05.015
- [25] LINHART, Igor. Toxikologie: interakce škodlivých látek s živými organismy, jejich mechanismy, projevy a důsledky. 1st edition. Praha: Vysoká škola chemicko-technologická, 2012. ISBN 978807800061
- [26] MASIH, Jamson, Raj SINGHVI, Aja TANUJA, Krishan KUMAR a Harison MASIH. Gaseous/particulate bound polycyclic aromatic hydrocarbons (PAHs), seasonal variation in North central part of rural India. *Sustainable Cities and Society*. 2012, **3**, 30-36. doi:10.1016/j.scs.2012.01.001
- [27] MENICHINI, E., N. LEONOVELLA, F. MONFREDINI a L. TURRIO-BALEASSARI. Relationships between indoor and outdoor air pollution by carcinogenic PAHs and PCBs. *Atmospheric Environment*. 2007, **41**(40), 9518-9529. doi:10.1016/j.atmosenv.2007.08.041
- [28] MOEINADDINI, Nazaher, Abbas ESMAILI SARI, Alireza RIYABI BAKHTIARI, Andrew Yiu-Chung CHAN, Seyed Mohammad TAGHAVI, Darryl HAWKER a Des CONNELL. Source apportionment of PAHs and n-alkanes in respirable particles in Tehran, Iran by wind sector and vertical profile. *Environmental Science and Pollution Research*. 2014, **21**(12), 7757-7772. doi:10.1007/s11356-014-2694-1
- [29] OHURA, Takeshi, Yuta KAMIYA a Fumikazu IKEMORI. Local and seasonal variations in concentrations of chlorinated polycyclic aromatic hydrocarbons associated with particles in a Japanese megacity. *Journal of Hazardous Materials*. 2016, **312**, 254-261. doi:10.1016/j.jhazmat.2016.03.072
- [30] OMAR, Nasr Yousef M.J, M.Radzi Bin ABAS, Kamal Aziz KETULY a Norhayati Mohd TAHIR. Concentrations of PAHs in atmospheric particles (PM-10) and roadside soil particles collected in Kuala Lumpur, Malaysia. *Atmospheric Environment*. 2002, **36**(2), 247-254. doi:10.1016/S1352-2310(01)00425-3
- [31] PEHNEC, Gordana, Ivana JAKOVLJEVIĆ, Anica ŠIŠOVIĆ, Ivan BEŠLIĆ a Vladimira VADIĆ. Influence of ozone and meteorological parameters on levels of polycyclic aromatic hydrocarbons in the air. *Atmospheric Environment*. 2016, **131**, 263-268. doi:10.1016/j.atmosenv.2016.02.009
- [32] PONGPIACHAN, Siwatt. Vertical Distribution and Potential Risk of Particulate Polycyclic Aromatic Hydrocarbons in High Buildings of Bangkok, Thailand. *Asian Pacific Journal of Cancer Prevention*. 2013, **14**(3), 1865-1877. doi:10.7314/APJCP.2013.14.3.1865
- [33] RE-POPPI, N a M SANTIAGO-SILVA. Polycyclic aromatic hydrocarbons and other selected organic compounds in ambient air of Campo Grande City, Brazil. *Atmospheric Environment*. 2005, **39**(16), 2839-2850. doi:10.1016/j.atmosenv.2004.10.006
- [34] STRAIF, Kurt, Aaron COHEN a Jonathan SAMET, ed. Air pollution and cancer (IARC Scientific Publications, 61) 150 cours Albert Thomas, 69372 Lyon Cedex 08, France: International Agency for Research on Cancer, 2013. ISBN 978-92-832-2166-1.
- [35] TAO, Shao Yi WANG, Shiming WU, et al. Vertical distribution of polycyclic aromatic hydrocarbons in atmospheric boundary layer of Beijing in winter. *Atmospheric Environment*. 2007, **41**(40), 9594-9602. doi:10.1016/j.atmosenv.2007.08.026
- [36] VAN VLIET, Patricia, Mirjam KNAPE, Jeroen DE HARTOG, Nicole JANSSEN, Hendrik HARSSEMA a Bert BRUNEKREEF. Motor Vehicle Exhaust and Chronic Respiratory Symptoms in Children Living near Freeways. *Environmental Research*. 1997, **74**(2), 122-132. doi:10.1006/enrs.1997.3757
- [37] VENKATARAMAN, Chandra, Salimol THOMAS a Pramod KULKARNI. Size distributions of polycyclic aromatic hydrocarbons—gas/particle partitioning to urban aerosols. *Journal of Aerosol Science*. 1999, **30**(6), 759-770. doi:10.1016/S0021-8502(98)00761-7
- [38] VISKARI, E.-L., R. REKILÄ, S. ROY, O. LEHTO, J. RUUSKANEN a L. KÄRENLAMPI. Airborne pollutants along a roadside: Assessment using snow analyses and moss bags. *Environmental Pollution*. 1997, **97**(1-2), 153-160. doi:10.1016/S0269-7491(97)00061-4
- [39] WU, S.P., S. TAO a W.X. LIU. Particle size distributions of polycyclic aromatic hydrocarbons in rural and urban atmosphere of Tianjin, China. *Chemosphere*. 2006, **62**(3), 357-367. doi:10.1016/j.chemosphere.2005.04.101
- [40] Act No. 201/2012 Sb.: Zákon o ochraně ovzduší. 2012, Příloha 1: Imisní limity, 69/2012.
- [41] Act No. 330/2012 Sb.: Vyhláška o způsobu posuzování a vyhodnocení úrovně znečištění, rozsahu informování veřejnosti o úrovni znečištění a při smogových situacích.
- [42] Česká meteorologická společnost: 20 let monitoringu kvality přírodního prostředí na observatoři Košetice. ČMeS, 2016, <http://www.cmcs.cz/cs/node/204> [2017-05-31].

- [43] Český hydrometeorologický ústav. (Czech Hydrometeorological Institute) ČHMÚ. 2015, <http://portal.chmi.cz/> [2017-05-19].
- [44] European Research Infrastructure for the observation of Aerosol, Clouds, and Trace gases: ACTRIS-2 IA in H2020. ACTRIS-2. 2015, <http://actris2.nilu.no/DataServices/ObservationalFacilities/AccessToObservationalFacilities.aspx> [2017-05-31].
- [45] IARC [International agency for research on cancer] monographs on the evaluation of the carcinogenic risk of chemicals to man. Lyon: International agency for research on cancer, 1976.
- [46] ICOS ATMOSPHERE THEMATIC CENTRE: Křešín near Pacov Observatory – Panel Board. ICOS, 2016, <https://icos-atc.lsce.ipsl.fr/KRE> [2017-05-31].
- [47] United States Environmental Protection Agency: US-EPA. US-EPA, 2017, <https://www.epa.gov/> [2017-05-31].
- [48] World Meteorological Organization: Global Atmosphere Watch. WMO, 2016, http://www.wmo.int/pages/prog/arep/gaw/gaw_home_en.html [2017-05-31].

RETRACTED