

STUDY OF AVAILABLE METHODS TO EVALUATE THE CONCENTRATIONS OF 16 POLYCYCLIC AROMATIC HYDROCARBONS (PAH) IN MINE WATERS FROM THE NORTH BOHEMIAN BROWN COAL BASIN

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ABSTRACT

Mine water samples from North Bohemian Brown Coal Basin (NBBCB), the Czech Republic, were tested. These mine waters were taken from the drilled hydrological wells in the mentioned NBBCB area. The purpose of the analysis was to find an available method to evaluate the concentration of 16 polycyclic aromatic hydrocarbons (PAH) using available equipment. Mine water samples were taken in February and April 2020 from the NBBCB area. Samples were first concentrated using Solid Phase Extraction (SPE). The extracts were then analyzed by high performance liquid chromatography (HPLC) in conjunction with the diode array detector (DAD) external standard method. The standard ISO 17993 was used in the analysis procedure, which was optimized for the HPLC/DAD system. The original detection limit of 0.005 µg/l set by the standard was adjusted to 0.0025 µg/l for 16 PAHs by optimizing the method. The total content of 16 PAHs ranged from values below the detection limit to 0.7315 µg/l. All concentrations were below the limit values for groundwater. The results showed that the mine waters from the NBBCB area are not contaminated with PAHs.

Keywords: Concentration of PAH; Diode array detector (DAD); High performance liquid chromatography (HPLC); Mine water; North Bohemian Brown Coal Basin (NBBCB).

1 INTRODUCTION

The North Bohemian Brown Coal Basin (NBBCB) is the largest sub-Ore Mountains basin and is located between the Ore Mountains, the Doupov Mountains and the Bohemian Central Mountains, the Czech Republic. The NBBCB area is rich in minerals. There are clays, claystones, sands, sandstones, gravels, but above all important deposits of brown coal [1]. Brown coal has been mined here since the 14th century. Surface lignite mining produces mine waters, which are all waters found in the mining area. The total amount, composition and temperature of mine waters depends on the depth of the quarry, on the hydrogeological conditions in the mining site and the chemical composition of the rocks through which the water penetrates into the mining areas. Mine waters are often highly aggressive, extremely yellow-brown, and reddish-brown, have a very low pH and, above all, are highly polluted. The source of mine water pollution is mainly their flow through the rock environment. These waters contain increased amounts of SO_4^{2-} , Fe^{2+} , Fe^{3+} ions and have an acidic pH – mainly due to the oxidation of iron sulphides (pyrite, marcasite) and the transition of their soluble components into solution. Waters that have been in contact with coal have, in addition to excessive amounts of iron, sulfur and other ions, also excessive amounts of dissolved and undissolved substances, such as coal dust and clay particles [2]. These waters can also be

contaminated with polycyclic aromatic hydrocarbons (PAH). PAHs are formed by the imperfect combustion of any carbon-containing materials. These are mainly combustion processes of almost all types of carbonaceous fuels. Within the NBBCB, the source of PAH can be current and historical coal seams and burning or former industrial generators for the production of flue gas [3]. In 1991, the government of the Czech Republic announced a reduction program for coal mining. Since then, less efficient mines have been gradually closed [4]. At present, it is possible that lignite mining in the NBBCB is in its final stages [5]. After this mining, the level of mine water could rise. Therefore, it is important to assess the quality of mine waters and decide on their possible use.

The impact of coal mining on mine water quality has been studied in [6–15]. Contamination of metals in water and sediments in areas of coal mines dealt studies for Poland [16,17], Australia [18] and India [19–23]. The overall quality of groundwater from coal mining in India (Brajrajnagar) was studied in [24]. The occurrence of polycyclic aromatic hydrocarbons (PAH) has been studied in surface soils from a coal mine in China (Huainan) [25]. In [26], NBBCB was studied for the impact of lignite mining on the environment. Metal contamination in soil and water samples near coal mines was evaluated [26]. However, the aim of this work is to find a suitable method to study the concentration of 16 PAHs in mine water samples from the NBBCB. This would make it possible to contribute additional parameters to the assessment of the quality and pollution of these mine waters.

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds found in air, soil, and water and are formed by imperfect combustion of organic materials, anthropogenic activity, natural losses or seepage from oil or coal deposits [27]. PAHs are potentially carcinogenic, mutagenic, and toxic to humans. Based on these adverse reactions, the United States Environmental Protection Agency (US EPA) has established 16 basic PAHs. These 16 PAHs with their toxic and genotoxic properties are shown in Table 1. Due to these toxic properties, PAHs were selected for this study. PAHs are commonly determined, for example gas chromatography with mass spectrometer (GC/MS) or high-performance liquid chromatography (HPLC) [28]. In this work, we used an HPLC system with a diode array detector (DAD) and an external calibration method to evaluate the concentration of PAH in mine waters from NBBCB. For this method, we performed a basic optimization to make the method suitable for mine water samples.

Table 1. List of 16 basic PAHs according to the US EPA with their basic toxic and genotoxic properties [29–31]

analyte	abbreviation	IARC group*	Genotoxicity	TEF**
naphthalene	NAPH	2B	Negative	0.001
acenaphthylene	ACY	not available	Questionable	0.001
fluorene	FLU	3	Negative	0.001
acenaphthene	ACE	3	Questionable	0.001
phenanthrene	PHEN	3	Questionable	0.001
anthracene	ANTH	3	Negative	0.01
fluoranthene	FLUO	3	Positive	0.001
pyrene	PYR	3	Questionable	0.001
chrysene	CHR	2B	Positive	0.01
benzo[a]anthracene	BaA	2B	Positive	0.1
benzo[b]fluoranthene	BbF	2B	Positive	0.1
benzo[k]fluoranthene	BkF	2B	Positive	0.1
benzo[a]pyrene	BaP	1	Positive	1
dibenzo[a,h]anthracene	DiAn	2A	Positive	1
indeno[123-c,d]pyrene	InPy	2B	Positive	0.1
benzo[g,h,i]perylene	BePe	3	Positive	0.01

*IARC group: 1 – the agent is carcinogenic to humans, 2A – the agent is probably carcinogenic to humans, 2B – the agent is possibly carcinogenic to humans, 3 – the agent is not classifiable as to its carcinogenicity to humans
 **TEF (Toxic Equivalency Factor): Each compound has a specific "toxic equivalency factor" (TEF). This factor indicates the degree of toxicity compared to 2,3,7,8-TCDD (reference dioxin), which is given a reference value of 1 [32].

2 MATERIALS AND METHODS

2.1 Mine water sampling from the NBBCB

Mine water samples were taken from boreholes drilled in the NBBCB. Specific places and depths of boreholes are given in Table 2. The wells were drilled by BauGeo s.r.o. Sampling was provided by the Institute of Inorganic Chemistry of the Academy of Sciences of the Czech Republic. Mine water samples were taken in February and April 2020 from drilled wells from the NBBCB area. The samples taken were immediately transferred to VSB – Technical University of Ostrava in 5l plastic bottles after collection. Here, for HPLC/DAD analysis, 1 l of the sample was filtered through a membrane filter with a porosity of 0.45 μm . The treated samples were visually described and stored in dark glass bottles in the dark and cold until analysis. The samples were analysed within 1 week after filtration.

Table 2. Location of the drilled wells in the NBBCB

Borehole number	Name borehole	Plot	Cadastral area	Coordinates S-JTSK *		Borehole depth [m]
				X	Y	
1	Jaroslav	603	Dubí-Bystrice	973045	777924	121
2	Wenzel	837/1	Teplice-Trnovany	975015	775767	50
4	Viktorin	647/7	Háj u Duchcova	977399	783517	81.5
7	Nelson III	297/10	Hrdlovka	978085	784873	223
8	Barbora	123	Hajniště u Duchcova	975264	782647	143
9	Pluto	572/3	Louka u Litvínova	979890	790698	347

*S-JTSK: System of unified trigonometric cadastral network

2.2 The principle of the analysis of mine water samples from the NBBCB

We used an HPLC system with a DAD detector for PAH analysis. Prior to the analysis itself, solid phase extraction (SPE) was performed on unknown mine water samples from the NBBCB, and the resulting eluents were evaporated under a stream of nitrogen to concentrate the sample. Unknown samples prepared in this way were subjected to HPLC/DAD analysis with an external standard (16 PAH standard mixture). We used the external standard method for the quantification of the analyte. We analyzed the external standard with a known concentration (16 PAH standard mixture) as well as mine water samples with an unknown concentration under the same conditions. We prepared the external standard in concentrations of 0.0025 $\mu\text{g/l}$; 0.009 $\mu\text{g/l}$; 0.055 $\mu\text{g/l}$; 0.1 $\mu\text{g/l}$; 1 $\mu\text{g/l}$. This gave a calibration curve (dependence of signal intensity on known concentration). We compared the resulting signal intensities of the unknown analyte (analyte peak area) with the results of the external standard (calibration curve) and thus determined the quantitative representation of the analyte in the unknown sample.

2.3 Experimental principle

The principle of the SPE method consists in concentrating the analytes on the SPE column from a large volume of liquid sample (100–1000 ml) to a small volume of elution solvent (5–10 ml). The SPE column is packed with a suitable adsorbent, for example octyl and quaternary amine group (C8 and C18), aminopropyl (NH₂), neutral alumina (ALN) or hydrophilic N-vinylpyrrolidone and lipophilic divinylbenzene (Oasis HLB). In our case, we used SPE colony type: Oasis HLB (Waters, Milford, MA, USA). A diagram of the individual steps of the SPE method is shown in Figure 1 [33]. The SPE column must first be activated (**conditioning**). Then, a large volume (100–1000 ml) of sample is poured through an SPE column in which the analyte is collected (**sample addition**).

The column is then washed with ultra-pure water to remove any polar components (**washing**). Finally, the SPE column is washed with elution solvent to release the trapped analyte (**elution**) [34].

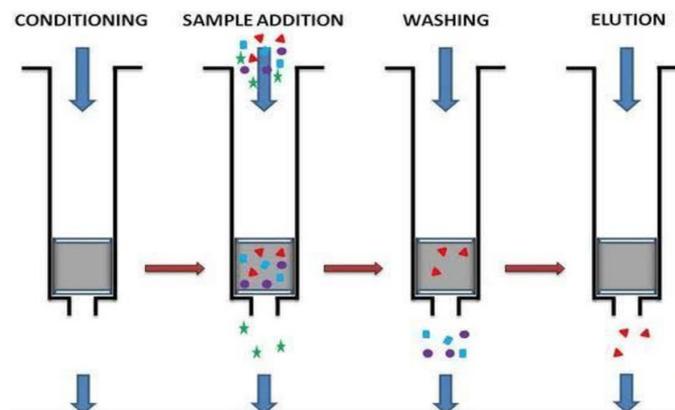


Figure 1. Individual steps of the SPE method [33]

The basic principle of high-performance liquid chromatography is the separation of analytes based on the different affinities of the given compounds for the mobile and stationary phases [35]. Different analytes have different distributions between the mobile and stationary phases and are therefore retained differently in the HPLC column. They then arrive at the detector at different retention times [36]. One of the types of detectors is the DAD detector. DAD is one of the UV / VIS detectors and allows to detect analytes at any wavelength [37]. Using a DAD detector, we analyzed substances that show an absorption spectrum in the ultraviolet or visible region [38]. The absorption of the analytes depends on the set wavelength of the DAD detector. For a given type of DAD detector, it is necessary to measure the absorption spectra of individual PAHs and determine the wavelengths at which the highest sensitivity is achieved for all analytes [39].

2.4 Experimental material and reagent

The 16 PAH standard mixture was purchased from NEOCHEMA GmbH and contains NAPH, ACY, FLU, ACE, PHEN, ANTH, FLUO, PYR, CHR, BaA, BbF, BkF, BaP, DiAn, InPy, BePe each at a concentration of 10 µg/ml. Dichloromethane, methanol, acetonitrile, and water for chromatography with high purity (HPLC LC-MS) were purchased from VWR International s.r.o.

2.5 Experimental method of SPE extraction and HPLC/DAD analysis

For the method of analysis of mine water samples, we used the standard ISO 17993. In this standard, the liquid-liquid extraction (LLE) method is used for sample preparation. Instead of this, we chose the solid phase extraction (SPE) method for our sample types. We selected the SPE method based on the results of the study [40]. In this study, we found that the SPE method is highly selective and sensitive for all 16 PAHs while LLE only for high molecular weight PAHs (BaA, BbF, BkF, BaP, DiAn, InPy, BePe). In addition, the SPE method is simpler, faster, cheaper, and safer (reduced consumption of often toxic solvents) [41].

In the case of the SPE extraction method, we used studies that, among other things, address the issue of the SPE procedure for the extraction of PAHs from a sample [40–42]. We found that for the needs and nature of our mine water samples, it was necessary to optimize these procedures (verify the suitability of the solvent, its volume, type of SPE column, etc.). This optimization is described in Section 3 Results and Discussion.

According to the ISO 17993 standard, it is recommended to use a mixture of acetonitrile and water for chromatography as the mobile phase for the analysis of PAHs using the HPLC system. We have maintained this mobile phase. However, it was necessary to optimize the flow rate of the mobile phase and to choose between

isocratic (mobile phase composition is constant during the analysis) and gradient elution (mobile phase composition is programmed during analysis). The results of this optimization are presented in Section 3 Results and Discussion. As a stationary phase, this standard recommends a chromatographic column that allows efficient separation of all 16 PAHs. We chose a Kinetex C 18 chromatographic column for analysis based on [28]. In our study, we verified that the Kinetex C 18 chromatographic column is suitable for efficient separation of 16 PAHs. For this system, it was necessary to optimize the parameters of HPLC analysis, especially the temperature of the column furnace and the injection volume of the sample. The results of this optimization are presented in Section 3 Results and Discussion. The ISO 17993 standard also uses a fluorescence detector (FLD) for the analysis of 15 PAHs. This detector cannot analyze ACY due to its weak fluorescence properties [28]. Therefore, we chose a spectrophotometric DAD detector for analysis, which allows for the analysis of all 16 PAHs according to the US EPA. For DAD detection, it was necessary to select the wavelengths at which the highest sensitivity is achieved for all 16 PAHs. The results of this optimization are presented below.

3 RESULTS AND DISCUSSION

3.1 Optimizing the analysis of 16 PAHs

For the needs of analysis of mine water samples, we had to optimize the procedures for SPE extraction of 16 PAHs and for the analytical method to determine the 16 PAHs using HPLC/DAD system, including the determination of suitable DAD detector wavelengths at which the highest sensitivity for 16 PAHs is achieved.

3.2 Optimization of SPE extraction method

For the needs of SPE extraction of 16 PAHs, we had to optimize these methods [41,42]. The SPE column Oasis HLB was satisfactory and proved also suitable for our mine water samples. The types of solvents were also satisfactory, only their volumes needed to be adjusted. The following solvents and their volumes were therefore chosen for the individual phases of SPE extraction:

- 1) Conditioning: 6ml dichlormethane, 6ml methanol and 6ml water for HPLC
- 2) Sample addition: 1 litre of mine water sample
- 3) Washing: 5 ml water for HPLC
- 4) Elution: 8 ml dichlormethane

After eluting the analytes from the SPE column, the samples were evaporated under a stream of nitrogen to a volume of 1 ml to concentrate the sample. The mine water samples prepared in this way were then analyzed using an HPLC/DAD system.

3.3 Optimization of HPLC/DAD analysis method

3.3.1 Optimization of HPLC analysis parameters

Analyses were performed using an Ultimate 3000 HPLC system: *SRD-3200* (Thermo Fisher Scientific, USA) (see Figure 2, part I), which consists of a binary gradient pump: *HPG-3200SD* (A), an autosampler: *WPS-3000TSL ANALYTICAL* (B), a column compartment: *TCC 3000SD* (C) and a DAD detector: *DAD-3000* (D). For the separation of PAH, we used an analytical column Kinetex C 18 with parameters 2.2 μm ; 120 \AA ; 2.1 x 100 mm (Thermo Fisher Scientific, USA) in combination with a 4x2 mm C18 precolumn (Phenomenex, USA) (see Figure 2 part II.). We kept the temperature of the column furnace constant at 20 $^{\circ}\text{C}$ throughout the analysis. As mobile phase, we used 80% acetonitrile in isocratic mode with a constant mobile phase rate of 0.2 ml / min. We chose a sample injection volume of 10 μl . The total analysis time was 35 minutes.

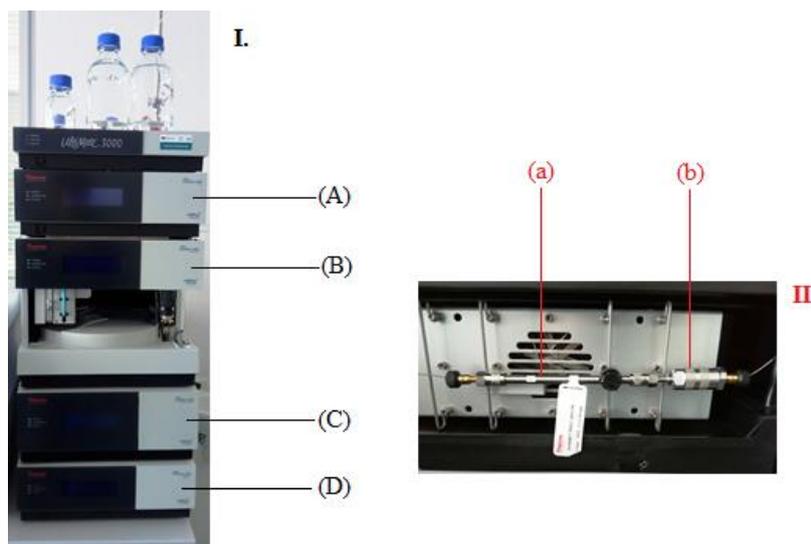


Figure 2. Ultimate 3000 HPLC system instrumentation (Thermo Fisher Scientific, USA) on the left (I.) and analytical column (a) and pre-column (b) on the right (II.)

3.3.2 Optimization of DAD detector parameters

Most PAHs have an absorption at 254 nm, but this is not a specific wavelength for all PAHs [39]. As part of the optimization of the method, we therefore had to measure the absorption spectra of individual PAHs and determine the wavelengths at which the highest sensitivity is achieved for all PAHs. We achieved good sensitivity for all analyzed PAHs at the set wavelengths of the DAD detectors 220, 254, 270 and 290 (see Figure 3). The specific wavelengths and retention times of all 16 PAHs are given in Table 3.

Table 3. Experimentally established wavelengths used to detect 16 PAHs with characteristic retention times

elution order	analyte	retention time [min]	specific wavelength [nm]
1	NAPH	3.0	220
2	ACY	3.3	220
3	FLU	4.0	270
4	ACE	4.2	220
5	PHEN	4.5	254
6	ANTH	4.8	254
7	FLUO	5.7	290
8	PYR	6.4	270
9	CHR	7.9	270
10	BaA	8.0	290
11	BbF	11.1	290
12	BkF	11.6	290
13	BaP	12.9	290
14	DiAn	15.0	290
15	InPy	18.3	254
16	BePe	18.7	290

Using the above selected wavelengths, we were able to distinguish FLU from ACE and CHR from BaA. Combining the wavelengths of 220 and 254 nm, we distinguished FLU from ACE. We see this in Figure 3 when we observed a sharp absorption peak for ACE at 220 nm, but at 254 nm we did not observe any absorption in contrast to FLU. In a similar way, we distinguished CHR from BaA using wavelengths of 270 and 290 nm (see Figure 4).

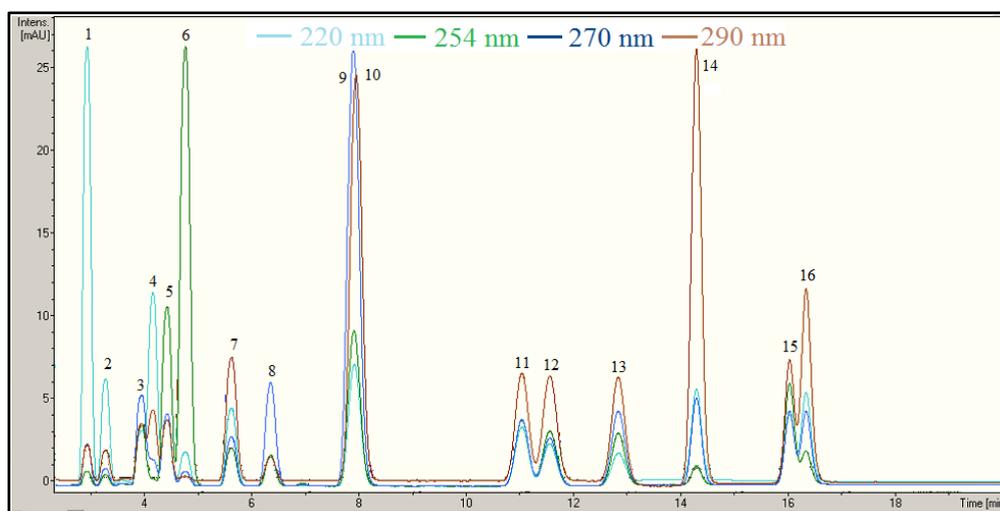


Figure 3. Experimental example of detection of 16 PAHs at set wavelengths of DAD detector 220, 254, 270 and 290 nm

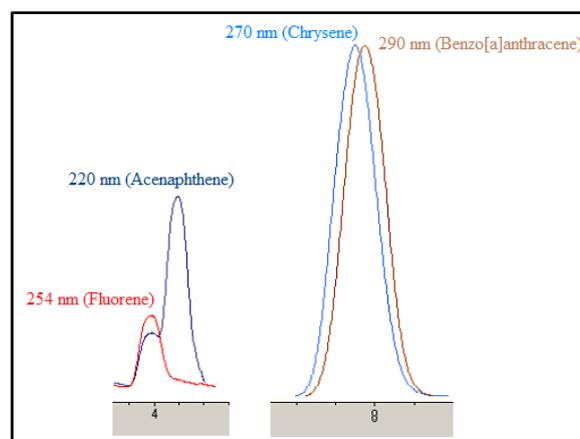


Figure 4. Experimental example of chromatograms between fluorene / acenaphthene and chrysene / benzo [a] anthracene pairs at given wavelengths of the DAD detector

3.4 Experimental results of optimized analysis of 16 PAHs

After optimizing the parameters of HPLC/DAD analysis (see above in Optimizing the Analysis of 16 PAHs), we reached a detection limit of 0.0025 µg/l for all 16 PAHs. Using this optimized method, we obtained the final analyte concentrations of mine water samples from the NBBCB from values below the detection limit up to 0.7315 µg/l. All these results are displayed in the Figures 5 and 6. It can be seen from these figures that the resulting concentrations of individual PAHs from the given wells in the two days of sampling slightly differ. This may be explained by the fact that the composition of mine waters changes over time. Therefore, it would be advantageous to continue with analyses.

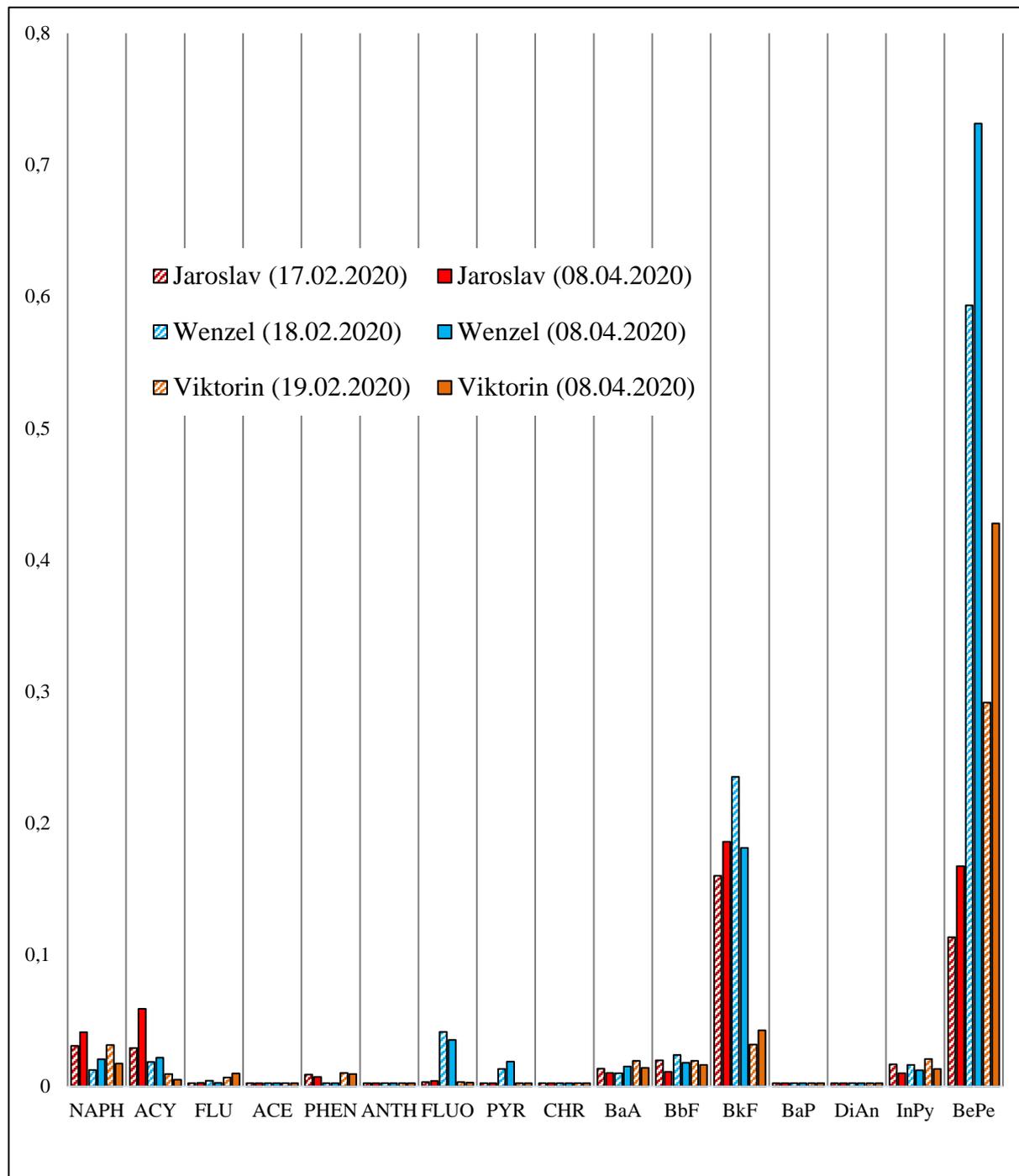


Figure 5. Resulting concentrations of 16 PAHs in mine water samples taken from boreholes in the NBBCB

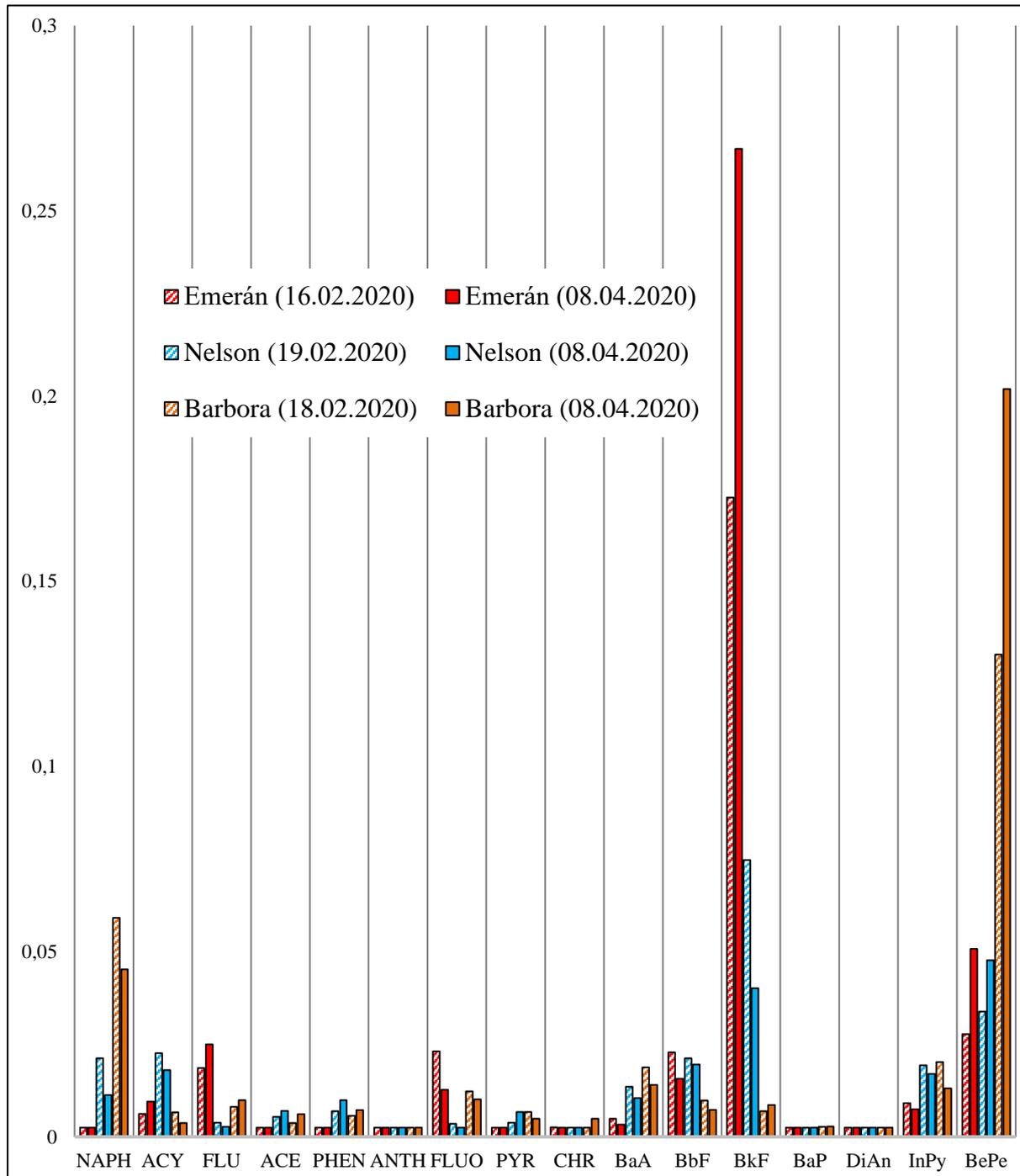


Figure 6. Resulting concentrations of 16 PAHs in mine water samples taken from boreholes in the NBBCB

The methodological guideline issued in the Bulletin of the Ministry of the Environment of the Czech Republic, year XIV-January 2014 – part 1 sets the limit concentrations of PAH (for PAH representatives according to US EPA except acenaphthylene, phenanthrene and benzo [ghi] perylene) for groundwater. These limits are listed below in Table 4 [43].

Table 4. Limit concentrations of PAHs for groundwater according to the Methodological Instruction of the Ministry of the Environment [43]

Analyte	Concentration [$\mu\text{g/l}$]
NAPH	0.14
ACY	-
FLU	220
ACE	400
PHEN	-
ANTH	1300
FLUO	630
PYR	87
CHR	2.9
BaA	0.029
BbF	0.029
BkF	0.29
BaP	0.0029
DiAn	0.0029
InPy	0.029
BePe	-

All measured concentrations of individual PAHs are below the limit set by the Ministry of the Environment of the Czech Republic and this can be seen in Figure 7. Mine waters from the selected wells in the NBBCB are therefore not contaminated with given PAHs and their concentration is minimal.

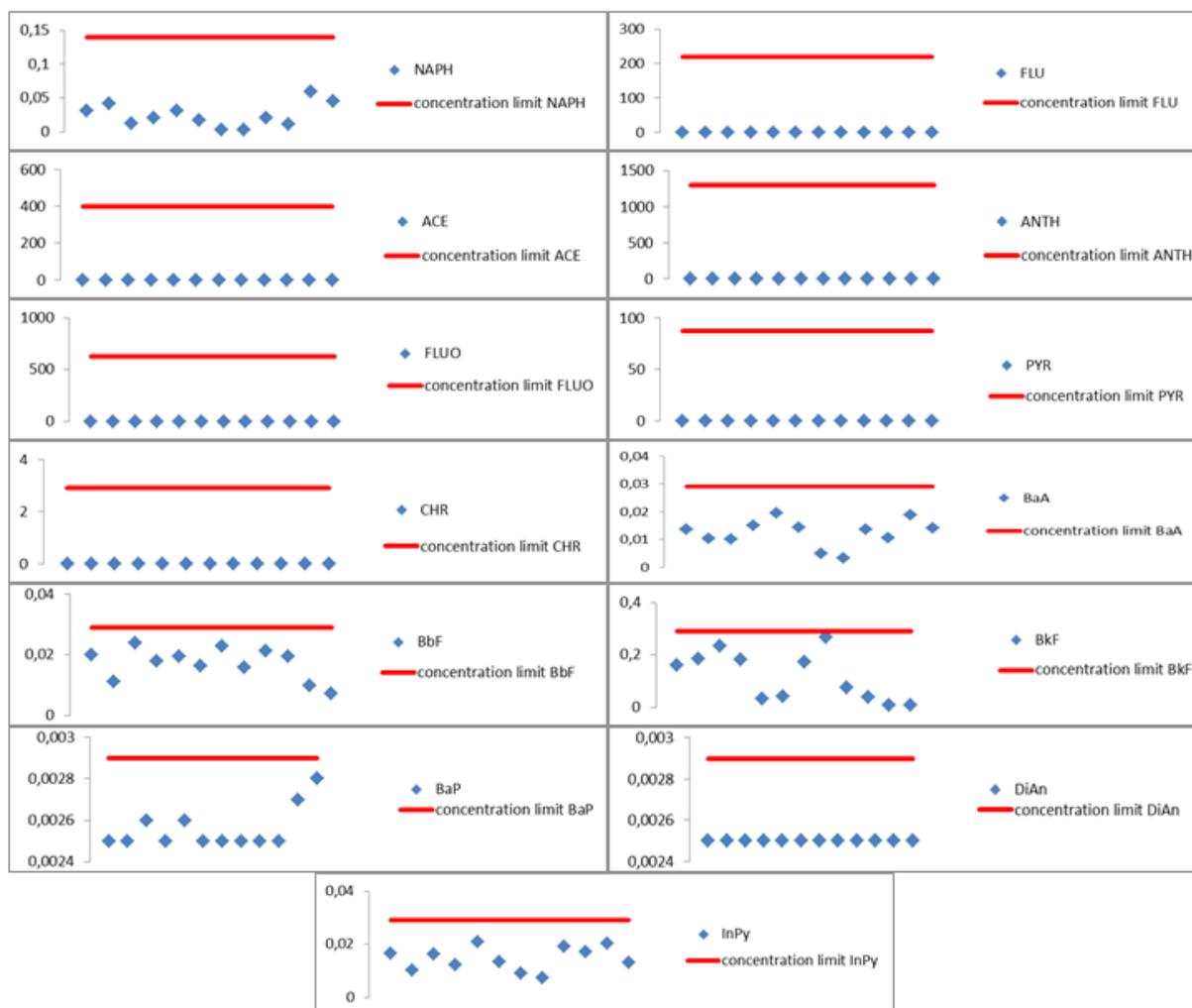


Figure 7. Comparison of the resulting measured values for individual representatives of PAHs with their limit concentrations (according to the Methodological Instruction of the Ministry of the Environment of the Czech Republic)

4 CONCLUSION

One of the discussed possibilities of using mine waters after the termination of brown coal mining in the NBBCB is their accumulation in the residual pits of quarries. The Podkrušnohorská basin belongs to the areas with above-average temperatures and very low levels of atmospheric precipitation [44,45]. The accumulation of water in the residual pits of the quarries, together with the appropriate reclamation of the area affected by mining and the revitalization of watercourses in this area, should offer a substantial improvement of the overall environment. For these purposes, it is important to control the quality of these waters. Although the experimental results of this study do not show PAH contamination in mine water samples from the NBBCB, this topic needs to be further developed. For example, to observe the concentration of PAH in mine water samples over a longer period of time and from multiple hydrological wells, and especially to monitor more parameters to determine the quality of water taken (total dissolved solids content (TDS), major ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , NO_3^- , Cl^- , F^- and HCO_3^-) and trace elements (B, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Cd, Ba and Pb), chlorides, nitrites, sulfates, etc.).

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