Macedonian Journal of Chemistry and Chemical Engineering, Vol. **42**, No. 1, pp. xx–xx (2023)

MJCCA9 – ISSN 1857-5552
e-ISSN 1857-5625

Received: July 26, 2022
Accepted: April 16, 2023

DOI: 10.20450/mjcce.2023.2552
Original scientific paper

POLYCYCLIC AROMATIC HYDROCARBONS IN TWO SEDIMENTARY ENVIRONMENTS OF THE TERTIARY KREPOLJIN COAL BASIN

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In the present study, statistical correlation analysis and multivariate statistical techniques (PCA/FA) were employed to investigate polycyclic aromatic hydrocarbons (PAHs) in sediments, such as illite-montmorillonite (IM) and calcite (Ct), from two sedimentary environments of the Tertiary Krepoljin brown coal basin in Serbia. The coal and sediment layers were formed in fresh-water bogs during the Lower Miocene period. The total amount of extractable PAHs was determined by gas chromatography with a triple quad mass detector (GC-MS-MS), and it ranged from 449 to 10585 μg l^{-1} in all sediments. Eight of the total 16 PAHs, which ranged from 175.17 to 658.42 μg l^{-1}, include benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene, and indeno[1,2,3-cd]pyrene, which are regarded as potentially carcinogenic, indicating a higher possibility of adverse ecological effects. Medium molecular-weight (MMW) PAHs were found to be predominant in all sediments. PAH concentrations are affected by several factors, such as carbon content, H/C mole ratio, and (less significant) O/C mole ratio. The non-existence of a correlation between the N/C ratio and other parameters indicates unspecific changes which accompany the original organic matter. The lower-sulfur Ct sediment samples were found to have a higher PAH content than higher sulfur IM samples, leading to the conclusion that the PAH content of sediments may be related to the depositional environment.

Keywords: illite-montmorillonitic environment; calcitic environment; polycyclic aromatic hydrocarbons; gas chromatography with a triple quad detector; multivariate statistical technique

ПОЛИЦИКЛИЧНИ АРОМАТИЧНИ ЈАГЛЕВОДОРОДИ ВО ДВЕ СЕДИМЕНТНИ СРЕДИНИ НА КРЕПОЛИНСКИОТ ТЕРЦИЈАРЕН ЈАГЛЕНОВ БАЗЕН

Во оваа студија се применети статистичка корелациона анализа и мултиваријантни статистички техники (PCA/FA) за да се истражат полицикличните ароматични јаглеводороди (PAHs), како што се илит-монтморилонит (IM) и калцит (Ct) во седименти, од две седиментни средини на терцијарниот креполински базен на лигнит во Србија. Јагленот и седиментните слоеви се формирани во слатководни мочуришта за време на периодот на долен миоцен. Вкупното количество на PAHs што можат да се екстрахираат беше одредено со гасна хроматографија со масен детектор со трократен квадрупол (GC-MS-MS) и беа во опсегот од 449 до 10585 μg l^{-1} во сите седименти. Осум од вкупно 16 PAHs рангирани од 175,17 до 658,42 μg l^{-1} содржат бензо[a]антрацен, хризен, бензо[b]флуорантен, бензо[k]флуорантен, бензо[a]пирен, дибензо[a,h]антрацен, бензо[g,h,i]перилен и индено[1,2,3-cd]пирен; Сите тие се сметаат за потенцијално канцерогени, укажувајќи на поголема веројатност за настанување несакани еколошки ефекти. Беше утврдено дека во сите седименти преовладуваат PAHs со средни молекулски тежини (MMW). Концентрациите на PAHs зависат од повеќе фактори, како што се содржината на јаглерод, молскиот однос на H/C и (помалку значајно) молскиот однос на O/C. Непостоењето на корелација меѓу односот на N/C и други параметри укажува на неспецифични промени што ја придружуваат оригиналната органска материја. Беше утврдено дека седиментните примероци на калцит со помала содржина на сулфур имаат поголема содржина на PAHs од примероците на IM со повисока содржина на сулфур што наведува на заклучок дека содржината на PAHs во седиментите може да е поврзана со опкружувањето при таложењето.

Клучни зборови: илитно-монтморилонитно опкружување; калцитно опкружување; полициклични ароматични јаглеводороди; гасна хроматографија со троен квадруполен детектор; мултиваријнтна статистичка анализа

1. INTRODUCTION

The three-dimensional network of coal is composed of condensed aromatic and hydroaromatic compounds which are connected via short alkyl bridges, ether linkages, and thioether linkages. Polycyclic aromatic hydrocarbons (PAHs) are an integral part of the coal structure. PAHs in coal/sediments are affected not only by coal rank but also by their origin, including depositional environment, precursor material, formation history, and geological age.[1–7]

PAHs are comprised of many carcinogenic substances and are ubiquitous in the environment. The U.S. Environmental Protection Agency regulates 16 priority pollutant PAHs (16 EPA-PAH) spanning from 2–6 condensed aromatic rings, which are commonly analyzed.

Organic geochemical characteristics of coal are frequently used to evaluate essential information regarding the coal-forming plant communities, depositional environment, and the maturity level of organic matter. Some common molecular parameters for saturated hydrocarbons can provide valuable information regarding the plant precursors, redox conditions during peatification, and the thermal evolution degree of organic matter. Similarly, the presence of aromatic molecules containing PAHs and heterocyclic aromatic compounds can also support geological information. PAHs have been reported in coals of different ranks,[8–10] and several studies have examined their occurrence modes, the origin of minerals in coal, and the organic matter content.[11–15] However, no study has yet described the characteristics of early diagenetic processes and the mineralogy composition of coal related to the concentration of extractable PAHs in a literature review.

Here we describe the sediments from the Krepoljin brown coal basin, which are exploited in the small mine in East Serbia. These coals are in a low maturity range with good preservation of organic compounds. The most impressive of these is the covering of the entire Tertiary sequence by Mesozoic (Triassic and Jurassic) limestones, having a thickness of up to 800 m, which occurred at the end of the Tertiary period. In addition, the entire basin is intersected by many bigger and smaller faults, resulting in massive, individual tectonic blocks. We characterized PAH profiles in two sedimentary environments in the Krepoljin coal basin. The samples of the intercalated mixed sediments (pieces of coal in clays, sandstones, and shales) originate from two hydrogeochemically differing sedimentary environments: the illite-montmorillonitic (IM) and the calcitic (Ct) environment. The characteristics of the early diagenetic processes which influenced the composition of the organic matter of this sediment was assessed by the statistical correlation analysis and multivariate statistical techniques. The results provide essential information for establishing and implementing sustainable and safe practices for managing and disposing of coals in the Krepoljin brown coal basin and other coal-polluted regions.

2. EXPERIMENTAL

2.1. *Study area and sampling*

The samples comprise the sedimentary sequences from the underlayers to the overlayers, including several sublayers of coal and the intercalated mixed sediments (clays and sandstones containing coal fragments). Tertiary sediments of the coal-bearing series of the Krepoljin basin consist of the lake sediments composed of clays, sands, gravels, argillites, (less often) marls, coal layers, and other deposits (Fig. 1). The underlayer of the coal bed has a changeable granulometric structure and consists of, more or less, clay-bearing, predominantly weakly bound soft sandstones and sands of greenish color. The thickness of underlayer section sediments (20–70 m) varies due to the degree of preservation and erosion of the Tertiary products. The presence of porous, so-called multicolored sandstone, maroon and less often yellow, is characteristic for the overlayer. Its maximum thickness goes up to 2 m. The continental-type coal bed of the freshwater lake sediment series comprises two coal seams. The lower coal seam, which is the main carrier of the coal reserves, has a regular spread in the whole bed (the contours of the bed) without losing minimum exploitation thickness. In contrast, the upper coal seam has limited thickening and minimal thickness. This coal-bearing section of the Miocene series could be found in the transgressive phase of the lake Aquatoria, marking the outset of the sedimentation cycle. Over the thin proluvial sediments, the bed stretches on an uneven, highly karstified paleorelief on which a configurational complex was formed during the continental phase before the Miocene. Concerning this feature, the existence of several peat-forming centers in the beginning can be hypothesized. These separate centers, growing vertically due to continuous sedimentation, progressively extended their area and finally became fused into a unique coal forming bed. Such sedimentation conditions at the beginning of the Miocene series had a considerable impact on the genesis of the bed, which has been manifested through the variability of the coal seam thickness. The horizontal component of tectonic changes was more prominent, and the basin was covered by powerful Triassic and Jurassic limestones which protected it from subsequent external influences. The Krepoljin zone has a karst structure, but it shows only some characteristics of overlap fault in the coal mine area. Fissures are prominent in the bed, while tectonic movements along the fissures have caused the appearance of a block structure with denivelated and disparately oriented blocks. The lower, i.e., the elder coal-bearing series from two exploratory boreholes, J-98 and J-99, of the Central Field-Block III were investigated.[16] A suite of 10 sediment samples was collected from the Tertiary Krepoljin brown coal basin in Serbia.

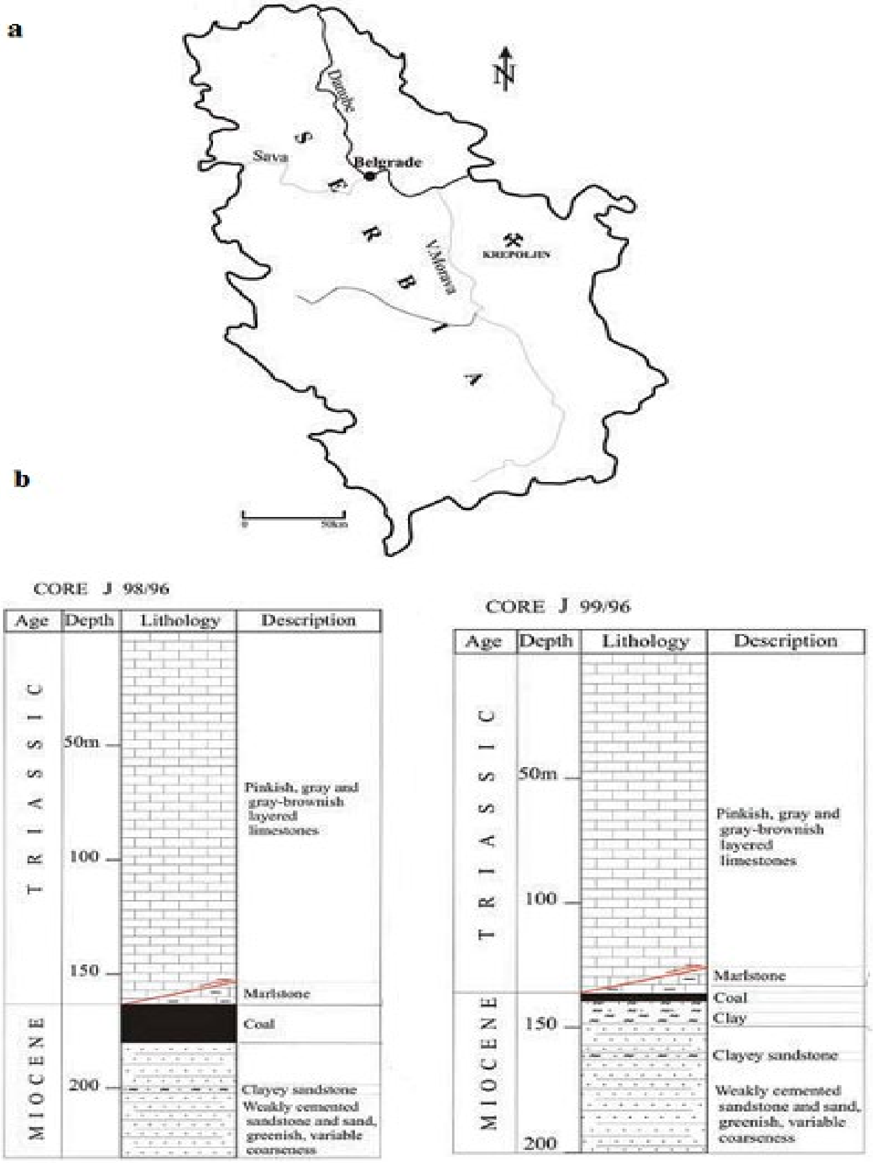

Fig. 1. Location of the study area and stratigraphic column of the studied area

2.2. *Mineralogical composition*

The approximate abundance of the main minerals in the mixed and the noncoal sediments was estimated by semiquantitative X-ray diffraction analysis using a Philips RW1710 diffractometer and APD software processing.

The differences in the composition of the principal mineral assemblages of individual members in the sedimentary sequences indicate the occurrence of hydrogeological events (e.g., changes in the sources of sedimentary material). Such events changed the hydrogeochemical conditions in the sequences of freshwater peat-bogs or lakes. Generally, two types of mineral assemblages can be recognized: the sediments with a clay mineral matrix and those with a calcitic matrix.

Sediments with a clay mineral matrix, IM. These sediments consist mainly of quartz and phyllosilicate clay minerals (illite, montmorillonite, kaolinite, and, sporadically, chlorite or halloysite). Several members also contain antigorite, micas, feldspars, phillipsite, or chaoite. In these sedimentary environments, due to the absence of carbonates, a relatively low pH can be expected, as well as strong sorption of humic electron-acceptors (EA) and donors (ED) on clay minerals.[16]

Sediment with a calcitic matrix. The striking characteristic of this group is the prevalent content of calcite. The second abundant mineral in all members is quartz, whereas two of the members also contain antigorite. The prevalent content of calcite, as a pH buffer of infinite capacity, was very probably supplying a consistently high pH in the early diagenetic environments of these members despite the intermediary forming humic substances as proton sources.[16]

Total organic carbon (TOC) content and proximate and ultimate analysis were performed according to the procedure in the paper.[17]

2.3. *Polycyclic aromatic hydrocarbons*

Samples taken for lipid analyses were collected. Ten samples were collected, and each sample was wrapped with foil and sealed in bags to prevent contaminants. The samples were dried in open air immediately after excavation. After being ground to 100 mesh size, approximately 120 g of each sample was Soxhlet-extracted with dichloromethane for 72 h. The total extract was concentrated on a rotary evaporator under reduced pressure and then transferred to a vial. After being weighed, the total extracts were fractionated by column chromatography (neutral alumina/silica gel, 1:2), successively eluting with *n*-hexane, dichloromethane/hexane mixture (30:70, v:v), and methanol to get the saturated hydrocarbons, aromatics, and polar fraction.

The concentrated aromatic extracts were analyzed using an Agilent Technologies gas chromatograph with a triple quad mass detector (GC-MS-MS) (7890B/7010, Agilent, USA) with an HP-5MS capillary column with 30 m × 0.25 mm × 0.25 μm film thickness. Helium (6.0, Messer) was used as a carrier gas at a constant flow rate of 1.5 ml min^{-1}. A 1 μl sample was injected in the splitless mode. The oven program was as follows: The temperature was increased from 50 °C to 200 °C at 25 °C/min, then to 320 °C at 5 °C/min; the. injector temperature was 300 °C.Samples were taken three times with an RSD of 3.12 %.

Internal standards used as controls were acenaften-d10, fenantren-d10, chrysene-d12, perylene-d12, and surrogate standards nitrobenzene-d5, 2-fluoro-1,1'-biphenyl, and *p*-terphenyl-d14.

All solvents (Sigma-Aldrich) were of a quality for gas chromatography. Reagent solutions were prepared with hexane/acetone 1:1, v:v. The solvents were used as supplied.

2.4. *Data processing*

Statistical data processing included application of multivariate statistical methods to previously systematized data in samples from Krepoljin sediment areas. Factor analysis was utilized, specifically analysis of the main components (PCA). PCA is used for the detection of intercorrelations within a set of data or for grouping variables that are mutually correlated. [18] The main goal of this technique is to extract a small number of factors that can explain the variation of a large amount of analytical data. The Kaiser–Meyer–Olkin (KMO) test and Bartlett's test of sphericity were used to check the sampling adequacy. For the PCA/FA, this was conducted through a correlation matrix using the Statistica software package for Windows, (Statsoft, Inc. 8.0) and the SPSS statistical package, version 20.0 for Windows (IBM Corporation, Armonk, NY).

3. RESULTS AND DISCUSSION

3.1. *Ultimate analysis and basic biomarker proxies*

The bulk geochemical parameters, which include the total organic carbon content (C_{org}), total sulfur content, organic sulfur, and mole ratios of H/C, O/C, and N/C, are given in Table 1.

Table 1

Mean values of 16 EPA PAHs, ultimate analysis, and total sulfur content with standard deviations for illite-montmorillonitic and calcitic environments

	c ± SD / μg l^{-1}	
	IM samples	Ct samples
Naphthalene	23.61 ± 0.16	23.63 ± 0.15
Acenaphthylene	31.95 ± 0.29	31.91 ± 0.13
Acenaphthene	29.48 ± 0.21	29.45 ± 0.24
Fluorene	25.69 ± 0.11	26.06 ± 0.69
Phenanthrene	43.99 ± 2.47	45.35 ± 3.88
Anthracene	16.73 ± 1.31	17.02 ± 1.98
Fluoranthene	94.16 ± 55.83	69.34 ± 56.20
Pyrene	93.02 ± 45.37	56.79 ± 31.87
Benzo[a]anthracene	152.52 ± 75.39	171.49 ± 93.01
Chrysene	68.84 ± 30.253	76.71 ± 36/66
Benzo[b]fluoranthene	20.85 ± 13.14	35.11 ± 33.58
Benzo[k]fluoranthene	33.45 ± 14.68	49.73 ± 38.16
Benzo[a]pyrene	37.95 ± 6.71	42.48 ± 33.10
Dibenzo[a,h]anthracene	12.80 ± 3.67	12.06 ± 20.67
Benzo[g,h,i]perylene	14.94 ± 0.75	17.55 ± 2.46
Indeno[1,2,3-cd]pyrene	7.49 ± 0.91	9.04 ± 3.00
Content of C_{org},	23.58 ± 10.54	14.36 ± 9.274
Ultimate analysis		
H/C molar ratio	1.156 ± 0.08	1.167 ± 0.178
O/C molar ratio	0.33 ± 0.041	0.57 ± 0.105
N/C molar ratio	0.012 ± 0.007	0.012 ± 0.003
Content of total S	346.98 ± 99.27	326.17 ± 56.28

The precursor material of higher plant gymnosperms significantly influenced the overall organic matter of mixed sediments in both hydrochemical environments. The OM of the sediments is composed mainly of polar compounds, over 53 wt. %, reflecting the low maturity of the sediments. The sample contains an abundance of long-chain *n*-alkanes (*n*-C17-C to *n*-C31) that exhibit a strong odd carbon preference. In the Ct-population, *n*-C27 dominates, while *n*-C29 alkane predominates in the I-M environment. According to maceral analyses, terrestrial precursors dominate, while algal ones are minor. The aromatic structures consist of compounds derived from the abietane type sceletion formed in anaerobic or a combination of aerobic and anaerobic processes: dehydroabietane, simonelite, and retene, with a predominance of simonelite and dehydroabietane.[17] Possible precursors for aromatic abietane type diterpenoids are pimarane and phyllocladane derivates. Because of the relatively young, Miocene age of coals and sediments, it should be expected that these early diagenetic influences are still noticeable.

3.2. *PAH distribution*

The mean ± standard deviation (SD) results of individual PAHs calculated from data collected on all 10 tested samples are shown in Table 1. An example of GC-MS-MS of PAHs is presented in Figure 2. The statistical summaries of the parameters analyzed using box and whisker plots are shown in Figure 3. These variations are important to recognize in environmental assessment in which the contributions of PAHs are derived from other sources. Fly, Pyr, BenzoaA, Chr, Total S, and organic matter showed the highest variance in distribution and large spatial variations, while low molecular weight PAHs, DBA, BenzoIP, Indenopyren, and mole ratios displayed homogenous distribution across the investigated boreholes of the Krepoljin basin. The range of PAH concentrations was from 7.494 μg l^{-1} for IndenoPyren to 171.49 μg l^{-1} for benzo[a]pyren (Table 1). The total concentration of PAHs in sediments ranged from 449.63 to 1058.83 μg l^{-1}, with a mean concentration of 712.99 μg l^{-1} (Table 1). The highest total PAH concentration was recorded in one Ct sample at 1058.3 μg l^{-1}. The remaining samples had similar total PAH concentrations of 675.6 ± 112.3 μg l^{-1}.

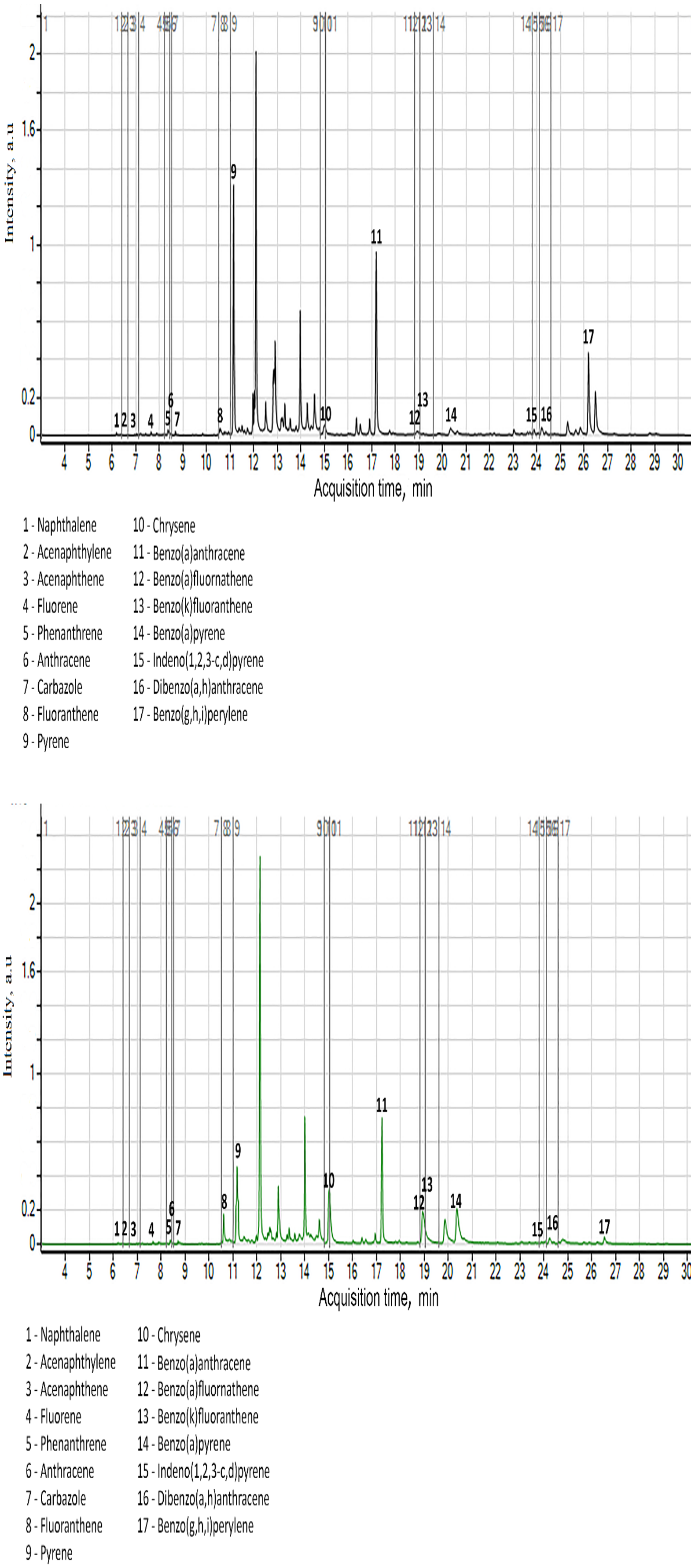

Fig. 2. GC-MS of 16 EPA PAHs of two different environmental sediments

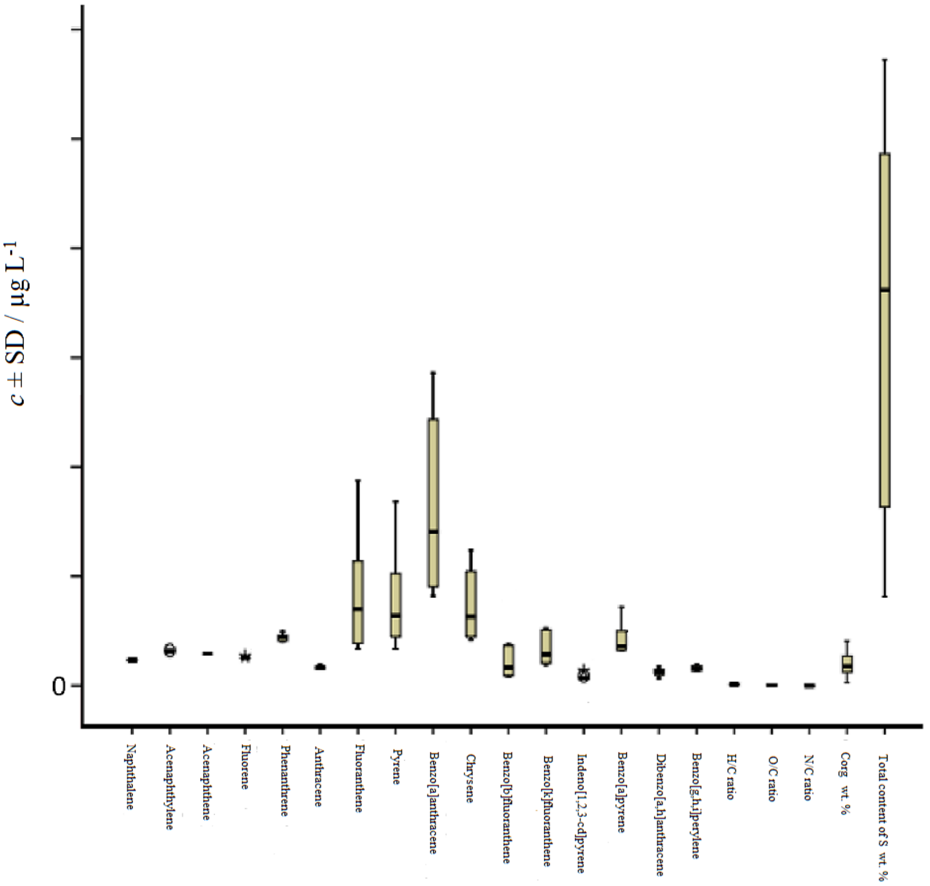

Fig. 3. Box and Whisker plot of PAHs, molal ratios, and total sulfur content in sediments of the Kreepoljin coal basin, with minimum, maximum, median, and 25 % and 75 % quartile values

A Pearson's correlation matrix was calculated in order to establish the relationships among PAHs and applied parameters and determine the common source in the Krepoljin coal basin. According to the values of the Pearson correlation coefficient, *s*, there is a positive correlation among them. Examples of significant correlations obtained in this paper are presented: naphthalene-acenaphthylene, $r = 0.732$**; naphthalene-acenaphthene, $r = 0.745$**; naphthalene-phenanthrene, $r = 0.799$**; naphthalene-anthracene, $r = 0.788$*; benzo[a]anthracene-chrysene, $r = 0.999$**; benzo[a]anthracene, $r = 0.802$**; benzo[a]anthracene-benzo[k]fluoranthene, $r = 0.\ 797$**; benzo[a] anthracene-benzo[a]pyrene, $r = 0.724$*; benzo[a] anthracene-dibenzo[a,h]anthracene, $r = 0.78$*; benzo[a]anthracene-benzo[g,h,i]perylene, $r = 0.699$*; chrysene-benzo[b]fluoranthene, $r = 0.799$**; chrysene- benzo[k]fluoranthene, $r = 0.794$**; chrysene-benzo[a]pyrene, $r = 0.726$**; benzo[b]fluoranthene-benzo[a]pyrene, $r = 0.715$**; benzo[b]fluoranthene-benzo[g,h,i]perylene, $r = 0.698$*; indeno[1,2,3-cd] pyrene-BkF, $r = 0.716$*; benzo[b]fluoranthene-indeno[1,2,3-cd]pyrene, $r = 0.71$*; benzo[a]pyrene-benzo[k]fluoranthene, $r = 0.714$* (*Statistically significant at $p < 0.05$, ** Statistically significant at $p < 0.01$).

The first component (PCA/FA) explains the most variance present in the dataset, with each subsequent component explaining progressively less variance.[19] Prior to the application of PCA/FA, standardization (*z*-scale) of the chemical parameters was carried out to render each of them dimensionless in order to eliminate potential bias toward a particular parameter of a different unit with high concentrations.[20] The Varimax rotation method was used to extract the principal components (PCs), considering eigenvalues > 1 as significant for interpretation. According to Liu et al., 2013[21], factor loading is classified corresponding to absolute loading values as 'strong' (> 0.75).

Factor F1 (32.8 % of variance) This is the most numerous group, and it includes carcinogenic PAHs and mole ratios of H/C and O/C (Table 2). According to Kalf's study, fluoranthene, pyrene, benzo[a]anthracene, and benzo[k]fluoranthene have stronger carcinogenesis and mutation than benzo[a]pyrene, marked as the most carcinogenic.

Table 2

Principal component analysis of 16 PAHs, C org., mole ratios, and total sulfur content

Component 1 32.80 %	Component 2 22.50 %	Component 3 16.23 %	Component 4 11.607 %
Benzo[a]anthracene	Naphthalene	Fly	Corg
+0.935	+0.826	+ 0.909	+0.775
Chrysene	Acenaphthylene	Pyrene	S
+0.936	+0.736	+0.899	+0.861
Benzo[b]fluoranthene	Acenaphthene		
+0.754	+0.764		
Benzo[k]fluoranthene	Fluorene		
+ 0.748	+ 0.749		
Benzo[a]pyrene	Phenanthrene		
+0.773	+0.941		
Dibenzo[a,h]anthracene	Anthracene		
+0.756	+0.956		
Benzo[g,h,i]perylene			
+0.748			
Indeno[1,2,3-cd]pyrene			
+0.884			
H/C ratio			
+0.879			
O/C ratio			
+ 0.725			

So, as much of the harm was thought to be from benzo[a]pyrene, attention must also be paid to the hazards of other EPA PAHs.[22] The total abundance of carcinogenic PAHs in the analyzed samples ranged from 165.55 to 550.42 µg l^{-1}. Our study showed that BaA was the major compound, accounting for approximately 22 % of total PAHs in sediments from the IM and Ct samples, Table 1. The mean concentration of BaA in sediments from the IM samples was 152.52 ± 75.394 µg l^{-1}, while in Ct samples it was 171.491 ± 93.01 µg $l^{-1,}$ indicating a higher possibility of occurrence of adverse ecological effect in addition to the other indicated PAHs by Kalf's study.[23] Several studies show that the levels and patterns of PAHs in coal are systematically tied to coal parameters determining its maturity, such as carbon content and the mole ratios.[24–26] The mole ratio of H/C is one of the most important parameters of the coalification degree. Our results were consistent with the studies.[10] They analyzed the effect of carbon content and mole ratios on PAH content in Chinese and American coals, and the relationships were fitted by a Gauss-fit. The effect of the mole ratio of H/C on carcinogenic PAH content in our samples is shown in Figure 4a. This effect results from changes in the chemical structures of organic compounds during the organic matter metamorphism and evolution process. Coal evolution is a continuous process of aliphatic hydrocarbon condensation. In this process, the volatile matter continues to decline during the separation of O elements, and the molar ratio of H/C continues to grow. Accordingly, the volatile matter and mole ratio of H/C can directly reflect the changes in PAHs in raw coal.[27] On the basis of the structural changes in the organic matter of coal, a low H/C ratio indicates a high degree of cyclization in coal structure (aromaticity), and a substantial amount of PAH can be detected in raw coal. Both hydrochemical environments have a high and similar content of H/C for organic matter. The H/C of IM samples (1.16 ± 0.08) and H/C in calcitic sediments (1.17 ± 0.18) indicate the degree of diagenetic changes in the original biomass The O/C ratio, which expresses reduction, i.e., the oxidation degree of sediment organic matter, indicates that the oxido-reduction conditions and/or specific diagenesis which took place in a relatively closed system of the Krepoljin coal basin had an effect on the distribution of PAHs. The connection between the O/C-ratio with other geochemical parameters listed in Table 1 was searched by correlation analysis. However, no significant correlations were found. The actual degree of oxidation of OM and the low degree of coalification (expressed by the O/C-ratio) of the calcitic environment (0.575 ± 0.105), characterized by the high oxidative activity of humic EAs, is significantly higher than the oxidation degree of OM in the clay-matrix environments (0.331 ± 0.041). The statistical meaning of the slightly positive tendency of O/C with carcinogenic PAHs shows that oxido-reduction conditions have influenced the distribution of carcinogenic PAHs (Fig. 4b) significantly less than the H/C ratio. The N/C ratio depends on the structure of the original biomass and the kind of processes imposed on it,[28] but it was not marked as significant by the component analysis for all analyzed samples.

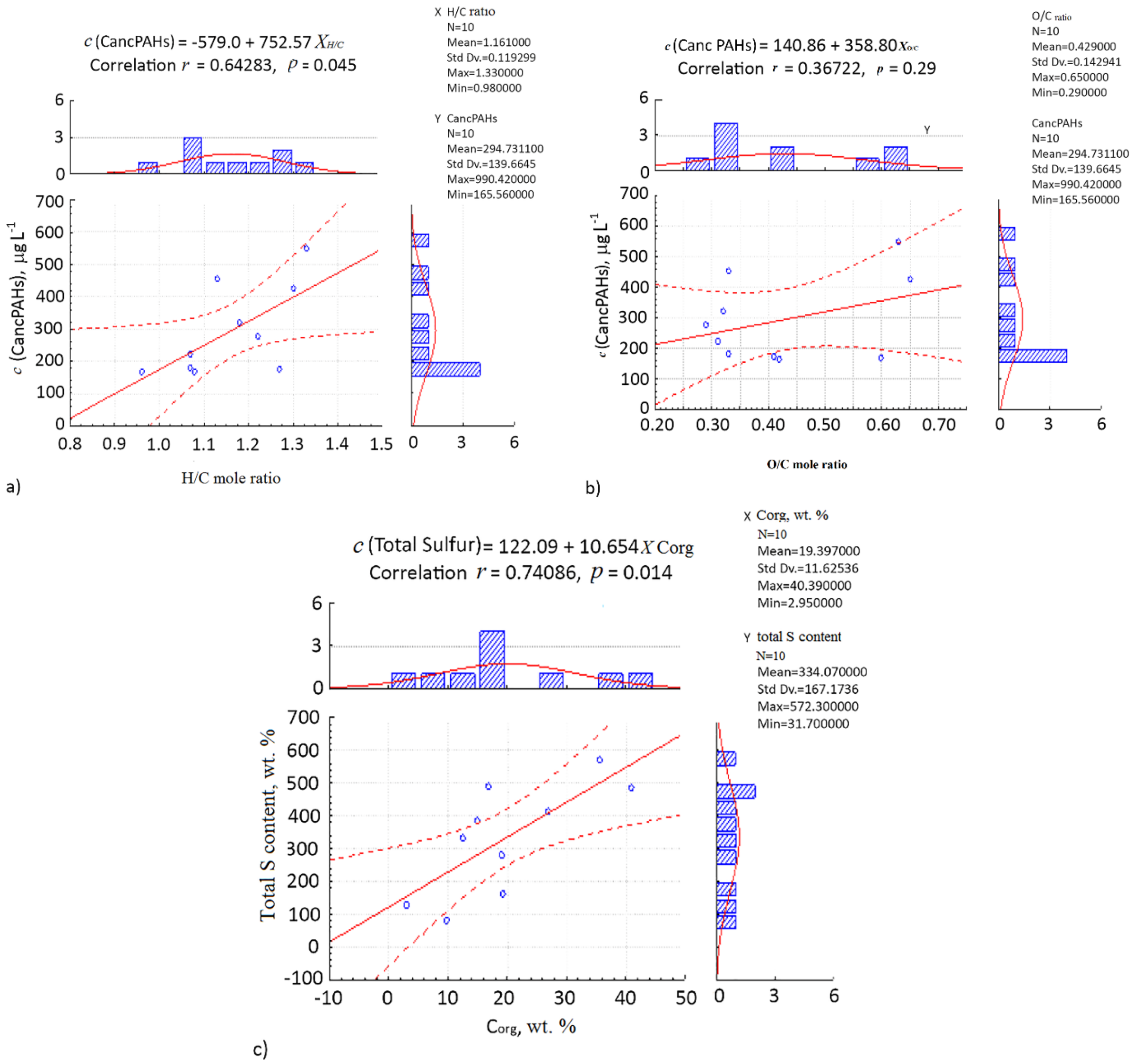

Fig. 4. Correlation diagrams: **a)** Canc. PAHs versus H/C ratio; **b)** Canc. PAHs versus O/C ratio; **c)** Corg versus total S.

Factor F2 (22.5 % of variance). A less numerous group consists of medium PAHs, Table 2. The 16-PAHs are divided into three groups according to their molecular weight, i.e., low-molecular-weight PAHs (LMW-PAHs), medium-molecular-weight PAHs (MMW-PAHs), and high-molecular-weight PAHs (HMW-PAHs). According to the division into groups, our samples are dominated by four-ring PAHs (MMW-PAHS) which contribute 46.4–64 % of the total (Fig. 5). The LMW PAHs species are dominating 16.2–37.9 % in most samples. Our results are consistent with the literature, which indicates the predominance of four-ring PAHs in the brown coal stage and the immaturity of the sedimentary organic matter.[29–30]

This two factor shows the diagenetic-maturation processes of the organic matter of mixed sediments, i.e., it results from the original biomass undergoing changes due to diagenetic transformations.

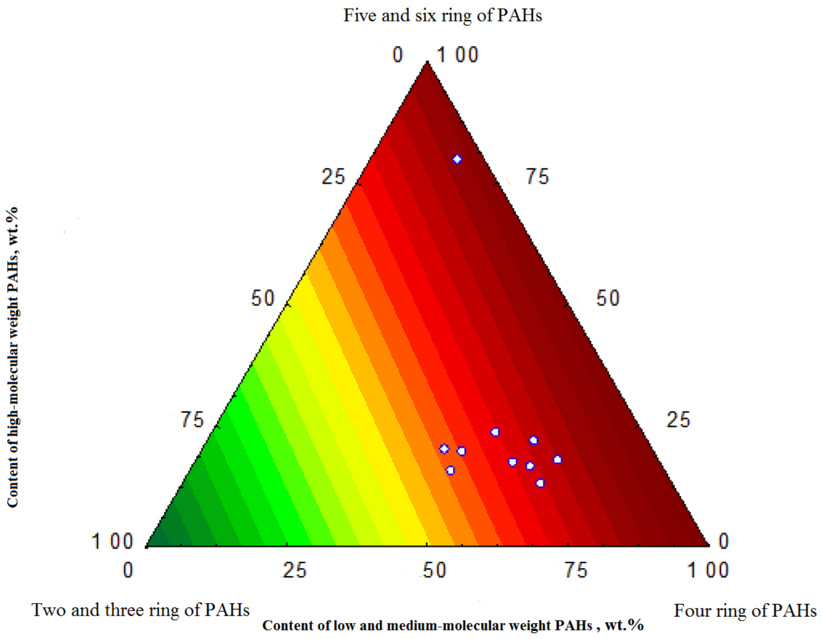

Fig. 5. Distribution of PAH groups in the ternary diagram

The third group, F3 (16.23% of variance). This group includes fluoranthene and pyrene, and it does not show any correlation, positive or negative, with the two previous groups. Fluoranthene and pyrene, both with a mass of 202, have the greatest range in stability and hence are good indicators of thermodynamic vs. kinetic processes. Fluoranthene is a structural isomer of the alternant PAH pyrene. It is not as thermodynamically stable as pyrene. Combustion and/or anthropogenic sources are usually deduced from an increase in the proportion of the less stable (kinetic) PAH isomer compared to the more stable (thermodynamic) isomer. The thermal alteration processes of organic matter are influenced by the inorganic sediment constituents. Slightly higher pyrene content was recorded in the IM environment (Fly/Pyr 0.906) compared to the calcitic group (Fly/Pyr 1.34, Fig. 6). Higher contents of fluoranthene and pyrene in the total PAHs are most likely a result of the participation of hydrocarbons of different origins (higher land plants/bacterial metabolite and/or specific diagenesis which occurred in the relatively closed system of the Krepoljin coal basin.

Factor F4 (15.544 % of variance). This factor is defined in the sediments by their content of organic carbon C_{org}, i.e., the whole organic matter expressed as C_{org} and total sulfur content, which are significantly correlated with each other (Table 2, Fig. 4c), and it indicates that the diagenesis of organic precursor materials was connected to diagenetic changes of sulfur species.

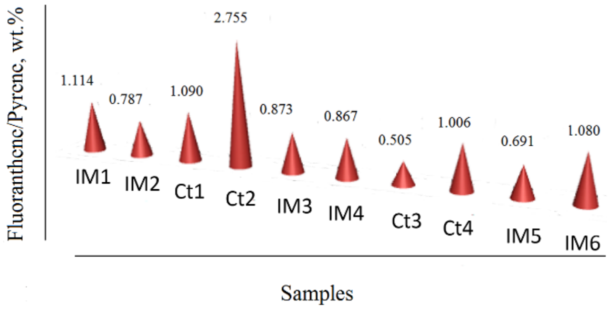

Fig. 6. Column diagram showing the distribution of the fluoranthene/pyrene ratio in different sediment (IM and Ct) samples

The C_{org} content in the samples varied from 9.74 % to 40.89 %. C_{org} content in the calcitic sediments (Ct) seems to be lower than in the clay-matrix IM sediments, but the difference is not statistically significant due to the wide range of individual values. The probable reasons for the low accumulation of precursor material during the formation of the these sediments (IM and CT) are as follows: a shallow water column in the bogs that led to the decomposition of a large amount of precursor material under aerobic conditions or lake flow resulting in an aerobic water column for the preservation and transformation of precursor materials into a continuous coal layer and coal fragments and other materials in the sediments were of an allochthonous origin, i.e., they were carried in with water from neighboring coal deposits. Carbonatic sediments have a weaker preservation capability for OM.[31] However, the apparent difference could contribute to (i) an initially differing rate of organic precursor material supply affected by the hydrogeological events which parallelly changed the source of mineral materials (introduction of carbonates instead of clays) and/or (ii) the higher oxidative activity of humic EAs in the Ct environment. From all of the above, there is no significant correlation ($r = 0.42$, $p = 0.22$) between PAHs and total organic carbon due to the wide range of individual values, which indicates that total organic carbon was a factor in PAH distribution in sediments.

The sulfur content in coal is widely regarded as an indicator of the paleoenvironmental conditions under which the precursor peat accumulated. The lower-sulfur Ct sediment samples have a slightly higher PAH content than higher sulfur IM samples, and this leads us to conclude that the PAH content of sediments may be related to the depositional environment, i.e., the lithology is determined primarily by the nature of the sediment input and by the conditions of deposition.[32] The poor correlation of total sulfur content with PAHs content ($r = 0.157$; $p = 0.66$) may result from the occurrence of other forms of sulfur: organic sulfur and inorganic sulfur, e.g*.*, pyrite that contribute to the total sulfur measured in the coals.[33–34]

4. CONCLUSIONS

The characteristics of the early diagenetic processes which influenced the composition of the PAHs of aromatic fraction from the Krepoljin brown coal basin of the Miocene age were assessed by chemometric techniques: statistical correlation analysis and multivariate principal component analysis.

The first two primary factors of principal component analysis define over 55.3 % of the total variance in the set of results, including carcinogenic PAHs, the mole ratios of H/C and O/C, and medium molecular weight PAHs, and show the diagenetic-maturation processes of organic matter. The total abundance of carcinogenic PAHs in the analyzed samples ranged from 165.55 to 550.42 $\mu g\ l^{-1}$. BaA was the major compound, accounting for approximately 22 % of the total PAHs in sediments from both hydrochemical environments. The molar ratio of H/C played a leading role in the change process of the PAHs, followed by the molar ratio of O/C. Samples were dominated by four-ring PAHs (MMW-PAHS), which contributed 46.4–64 % of the total PAHs. The mineral part had a decisive role in the processes of thermal alteration of fluoranthene and pyrene.

The average C_{org}-content in the calcitic sediments (Ct) seems to be lower than in the clay-matrix IM sediments, but the difference is not statistically significant due to the wide range of individual values. The non-existence of a correlation between the N/C ratio and other parameters indicates unspecific changes which accompany the original organic matter. The low-sulfur samples have a higher PAH content than the high-sulfur samples, leading to the conclusion that the PAH content of coals may be related to the depositional environment.

Acknowledgments. The authors thank the Ministry of Science, Technological Development and Innovation of Republic of Serbia (Grant No: **451-03-47/2023-01/200026**) for financial support.

REFERENCES

(1) Radke, M.; Wollisch, H.; Teichmüller, M., Generation and distribution of aromatic hydrocarbons in coals of low rank*. Org. Geochem.* **1990***, 15*, 539–563. https://doi.org/10.1016/0146-6380(90)90101-5

(2) Achten, C.; Hofmann, T., Native polycyclic aromatic hydrocarbons (PAH) in coals – a hardly recognized source of environmental contamination. *Sci. Total Environ.* **2009**, *407*, 2461–2473. https://doi.org/10.1016/j.scitotenv.2008.12.008

(3) Dameng, L.; Zhihua, L.; Yunyong, L., Distribution and occurrence of polycyclic aromatic hydrocarbons from coal combustion and coking and its impact on the environment. *Energy Procedia.* **2011,** *5*, 734–741. https://doi.org/:10.1016/j.egypro.2011.03.129

(4) Laumann, S.; Micić, V.; Kruge, A. M.; Achten, C.; Sachsenhofer, R. F.; Schwarzbauer, J.; Hofmann, T., Variations in concentrations and compositions of polycyclic aromatic hydrocarbons (PAHs) in coals related to the coal rank and origin. *Environ. Pollut.* **2011**, *159*, 2690–2697. https://doi.org/10.1016/j.envpol.2011.05.032

(5) Baran, A.; Tarnawski, M.; Urbański, K.; Pawlas, A.; Spalek, I., Concentration, sources and risk assessment of PAHs in bottom sediments. *Environ Sci Pollut Res.* **2017***, 24*, 23180–23195. https://doi.org/10.1007/s11356-017-9944-y

(6) Lawal, A., Polycyclic aromatic hydrocarbons. A review, *Cogent Environmental Science* **2017,** *3*, 1–89. https://doi.org/10.1080/23311843.2017.13398417

(7) Ciesielczuk, J.; Fabiańska, M. J.; Misz-Kennan, M.; Jura, D.; Filipiak, P.; Matuszewska, A., The disappearance of coal seams recorded in associated gangue rocks in the SW part of the Upper Silesian Coal Basin, Poland. *Minerals.* **2021***, 11*, 1–30. https://doi.org/10.3390/min11070735

(8) Xue, J.; Liu, G. J.; Niu, Z. Y.; Chou, C. L.; Qi, C.; Zheng, L. G.; Zhang, H. Y., Factors that influence the extraction of polycyclic aromatic hydrocarbons from coal. *Energy Fuels.* **2007**, *21*, 881–890. https://doi.org/10.1021/ef0605753

(9) Stout, S. A.; Emsbo-Mattingly, S., Concentration and character of PAHs and other hydrocarbons in coals of varying rank – Implications for environmental studies of

soils and sediments containing particulate coal. *Org. Geochem.* **2008**, *39*, 801–819. https://doi.org/10.1016/j.orggeochem.2008.04.017

(10) Wang, L.; Liu, G.; Zhang, J.; Chou, C. L.; Liu, J., Abundances of polycyclic aromatic hydrocarbons (PAHs) in 14 Chinese and American coals and their relation to coal rank and weathering. *Energy Fuels.* **2010**, *24*, 6061–6066. https://doi.org/10.1021/ef1010622

(11) Ward, C. R. Analysis and significance of mineral matter in coal seams. *Int. J. Coal Geol.* **2002** *50*, 135–168.

(12) Ketzer, M.; Holz, M.; Morad, S. Al-Aasm, S., Sequence stratigraphic distribution of diagenetic alterations in coal-bearing, paralic sandstones: evidence from the Rio Bonito formation (early Permian), southern Brazil. **2003.** https://doi.org/10.1046/j.1365-3091.2003.00586.x

(13) Liu, L;. Liu, Q.; Li, Y., Occurrence of iron in the minerals of carboniferous coal gangue of the Pingshuo open-pit mine, North China. *Clays Clay Miner.* 2022. *70*, 695–711. https://doi.org/10.1007/s42860-022-00211-7

(14) Yuan, L.; Huang, W.; Jiu, B.; Sun, Q.; Che, Q., Modes of occurrence and origin of minerals in Permian coals from the Huainan Coalfield, Anhui, China. *Minerals.* **2022** *10,* 399. https://doi.org/10.3390/min10050399

(15) Ciesielczuk, J.; Górka, M.; Fabiańska, M. J.; Misz-Kennan, M.; Jura, D., The influence of heating on the carbon isotope composition, organic geochemistry and petrology of coal from the Upper Silesian Coal Basin (Poland): An experimental and field study. *International Journal of Coal Geology* **2021** *241*, 103749. https://doi.org/10.1016/j.coal.2021.103749

(16) Dević, G., An Assessment of the chemical characteristics of early diagenetic processes in a geologically well-defined brown coal basin. *Energy Sources,* Part A*: Recovery, Utilization, and Environmental Effects*, **2015**, *37*, 2559–2566. https://doi.org/10.1080/15567036.2012.72414

(17) Devic, G.; Popovic, Z., Biomarker and micropetrographic investigations of coal from the Krepoljin brown coal basin serbia. *Inter. J. Coal Geol.* **2013***, 105*, 48–59. https://doi.org/10.1016/j.coal.2012.11.010

(18) Kruge, M. A., Determination of thermal maturity and organic matter type by principal components analysis of the distributions of polycyclic aromatic compounds. *Int. J. Coal Geol.* **2000,** *43*, 27–51. https://doi.org/10.1016/S0166-5162(99)00053-1

(19) Howarth, R. J.; Garrett, R. G., Statistical analysis and data display at the Geochemical Prospecting Research Centre and Applied Geochemistry Research Group, Imperial College, London. *Geochemistry Exploration Environment Analysis,* **2010,** *10*, 289. https://doi.org/10.1144/1467-7873/09-238

(20) Herojeet, R.; Rishi, M.; Lata, R.; Sharma, R., Application of environmetrics statistical models and water quality index for groundwater quality characterization of alluvial aquifer of Nalagarh Valley, Himachal Pradesh, India. *Sustainable Water Resources Management*. **2016** *2*, 39. https://doi.org/10.1007/s40899-015-0039-y

(21) Liu, C. W.; Lin, K. H.; Kuo, Y. M., Application of factor analysis in the assessment of groundwater quality in a blackfoot disease area in Taiwan. *Sci. Total Environ.* **2013***, 442*, 77–89. https://doi.org/10.1016/j.scitotenv.2012.10.045

(22) Ugochukwu, U. C.; Onuorah, L.; Okwu-Delunzu, V. U.; Odinkonigbo, U. E.; Onuora, O. H., Effects of power station and abattoir on PAH input into sediments of Oji River: ecological and human health exposure risks. *Environ. Monit. Assess.* **2019***, 191*, 775–779. https://doi.org/10.1007/s10661-019-7917-y

(23) Kalf, D. F.; Crommentuijn, T.; Van de Plassche, T. E. J., Environmental quality objectives for 10 polycyclic aromatic hydrocarbons (PAHs). E*cotoxicology and Environmental Safety*, **1997**, *36*, 89–97. https://doi.org/10.1006/eesa.1996.1495

(24) Stout, S. A.; Uhler, A. D.; McCarthy, K. J.; Emsbo-Mattingly, S., Chemical Fingerprinting of Hydrocarbons. In *Introduction to Environmental Forensics;* Academic Press, San Diego, 2002, pp. 137–260.

(25) Laumann, S.; Micić, V.; Kruge, M. A.; Achten, C.; Sachsenhofer, R. F.; Schwarzbauer, J.; Hofmann, T., Variations in concentrations and compositions of polycyclic aromatic hydrocarbons (PAHs) in coals related to the coal rank and origin. *Environ. Poll.* **2011,** *59*, 2690–2697. https://doi.org/10.1016/j.envpol.2011.05.03

(26) Fang, R.; Li, M.; Wang, T. G.; Zhang, L.; Shi, S., Identification and distribution of pyrene, methylpyrenes and their isomers in rock extracts and crude oils. *Org. Geochem.* **2015,** *83–84*, 65–76. http://dx.doi.org/10.1016/j.orggeochem.2015.03.014

(27) Verma, S. K.; Masto, R. E.; Gautam, S.; Choudhury, D. P.; Ram, L. C.; Maiti, S. K.; Maity, S., Investigations on PAHs and trace elements in coal and its combustion residues from a power plant. *Fuel.* **2015***, 162*, 138–147. https://doi.org/10.1016/j.fuel.2015.09.005

(28) Praus, P., Principal component weighted index for wastewater quality monitoring. *Water.* **2019***, 11,* 2–13. https://doi.org/10.3390/w11112376

(29) Yao, P.; Zhao, B.; Bianchi, T.; Guo, S.; Zhao, Z.; Li, M. Remineralization of sedimentary organic carbon in mud deposits of the Changjiang Estuary and adjacent shelf: Implications for carbon preservation and authigenic mineral formation. *Continental Shelf Res.* **2014**, *91*, 1–11. https://doi.org/:10.1016/j.csr.2014.08.010

(30) Bojakowska I.; Sokołowska, G., Polycyclic aromatic hydrocarbons in materials of burned peatlands. *Geol. Quart,* **2003**, *45*, 401–408. http://www.pjoes.com>pdf-87573-21432

(31) Taguchi, K.; Hasegawa, K.; Suzuki, T., The relationship between silica minerals and organic matter diagenesis: Its implication for the origin of oil. *Org.Geochem.* **1988,** *13*, 97–107. https://doi.org/10.1016/0146-6380(88)90030-7

(32) Asfahani, J.; Al-Hent, R.; Aissa, M., Identifying spectrometric signatures of phosphate deposits and enclosing sediments in Al-Awabed area, Northern Palmyrides, Central Syria, by the use of statistical factor analysis. *Appl Radiat Isot.* **2006***, 64*, 1082–1090. https://doi.org/10.1016/j.apradiso.2006.05.001

(33) Amrami, A.; Aizenshtat, Z., Mechanisms of sulfur introduction chemically controlled: δ34S imprint. *Org. Geochem.* **2004***, 35*, 1319–1336. https://doi.org/ 10.1016/j.orggeochem.2004.06.019

(34) Tang, Y. G.; Li, R.; Wang, S., Research progress and prospects of coal petrology and coal quality in China. *Int. J. Coal Sci. Technol.* **2020***, 7*, 273–287. https://doi.org/10.1007/s40789-020-00322-3