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HENRYK R. PARZENTNY<sup>1\*</sup>, LEOKADIA RÓG<sup>2</sup>**INITIAL ASSESSMENT OF VARIABILITY IN THE MODES OF OCCURRENCE  
OF SOME TRACE ELEMENTS IN COAL SEAMS WITH VERTICAL PROFILES  
IN THE UPPER SILESIA COAL BASIN IN POLAND**

Knowledge of the way in which minor and trace elements occur in coal is one of the most important geochemical indicators of coal quality. The differences between the methods of binding elements in coal in each coal seam and the variability of this feature of coal in the basin profile have not been discussed so far. These coal features were identified in a group of selected coal seams (209, 401, 405, 407, 501, 504, 510, 615, 620) in the Upper Silesian Coal Basin (USCB). At the same time, the differences in the role of identified mineral and maceral groups in concentrating specific elements in coal is highlighted. Identical or similar tendencies of changes in the way in which As and V, Ba and Rb, Co and Pb, Co and Zn, Mn and Pb, Pb and Zn, Co and Rb, and for Cr and Cu occur in the coal seams in the USCB profile was found. Changes in the mode of occurrence of As and Pb in coal in the USCB profile were probably influenced by carbonate mineralization. The changes in the mode of occurrence of Mn and Pb in the coal were probably determined by diagenetic sulfide mineralization, while the content of Ba, Cr, Rb, Sr, and V in coal from these deposits was affected by clay minerals. It was observed that the greater the degree of the carbonization of the organic matter of coal, the lower the content of As, Mn and Pb in coal and the higher the content of Ba and Sr in coal.

**Keywords:** mode of occurrence, trace elements, variability, bituminous coal, USCB

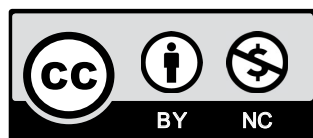
## 1. Introduction

Generally, the average content of minor and trace elements in bituminous coal in the world is known (i.a. Ketris & Yudovich, 2009; Swaine, 1990). Regularities in the lateral and vertical variability of element content within coal basins, deposits as well as lithostratigraphic series

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(i.a. Parzentny, 1994; Yudovich & Ketris, 2005) have frequently been reported. Among the geochemical features of coal, modes of element occurrence in coal are equally as important as the content of elements in coal (i.a. Finkelman et al., 2018; Kokowska-Pawłowska, 2014, 2016; Krzeszowska, 2019). Both features of coal have a decisive impact on the assessment of the suitability of coal for its mechanical and thermal processing, especially from an ecological perspective (i.a. Zhang et al., 2003; Zhou et al., 2018).

During the storage, enrichment and combustion of coal, a large proportion of elements present in coal can be released into the environment. Knowledge of the content and distribution of ecotoxic elements in coal may facilitate the determination of the degree of enrichment or depletion of these elements in fly ash, slag/bottom ash and in coal pyrolysis products. It may also enable the forecasting of the efficiency of leaching elements from coal and from solid coal combustion products. Moreover, it has a significant impact on the behaviour of elements during coal conversion and weathering (i.a. Bhangare et al., 2011; Hower et al., 2016; Pan et al., 2018; Xu et al., 2003; Zhao et al., 2018; Zhou et al., 2019).

Changes in coal quality affect, among others, the variable efficiency of enrichment, extraction and the possible recovery of critical elements from coal, from its enrichment waste and from combustion waste produced in power plants (Dai et al., 2018; Hower et al., 2018; King et al., 2018; Makowska et al., 2014; Strugała et al., 2014). It is also very important to know how minor and trace elements occur, especially critical and ecotoxic elements in coal, separately for each coal seam in a deposit or in a coal basin. This information may affect the decision of whether coal from coal seams qualifies for mining and thermal processing.

The authors wish to present the assess changes in the affinity of some trace elements in mineral matter and organic matter in coal and the differences in the probable role of groups of macerals and groups of minerals in concentrating elements in coal in the vertical sequence of several coal seams in the Upper Silesian Coal Basin. It is the largest and most resourceful Carboniferous coal basin in Poland with regard to bituminous coal. The geological characteristics of coal deposits and coal seams occurring in the USCB have been described by Jureczka and Kotas (1995).

## 2. Materials and methods

The study included 46 bituminous coal samples representing 9 selected coal seams (i.e. 209, 401, 405, 407, 501, 504, 510, 615 and 620) in the USCB. The samples were collected from areas of closed and active mines (mines: Barbara-Chorzów, Brzeszcze, Budryk, Grodziec, Halemba, Jankowice, Jowisz, Guido, Kazimierz-Juliusz, Katowice-Kleofas, Knurów, Mysłowice, Marcel, Niwka-Modrzejów, Pokój, Porąbka-Klimontów, Rydułtowy, Śląsk, Saturn, Staszic, Wieczorek, Wujek). Coal samples were taken from the entire thickness of the seams (according to PN-G-04501:1998 standard), which are characterized by a large and relatively constant thickness, large lateral spread and occurrence within at least 4 coal mines. The location of mines in the USCB area was presented by Jureczka et al. (2005).

The petrographic composition (i.e. the content of macerals of the vitrinite, liptinite and inertinite groups, the total content of mineral matter, and the content of clay, carbonate, sulphide and quartz minerals) and coal reflectance were determined using a Zeiss Axio Imager D1m microscope, (40× objective, 10× oculars, and 546-nm interference filters, reflected white light, immersion oil). The analysis was carried out in accordance with the standards set out in ISO 7404-3 (2009) and PN-ISO 7404-5 (2009). Ash yields were determined according to PN-ISO 1171:2002. The final

analyses included the determination of the content of fixed carbon (according to PN-G-04571:1998 standard), sulphate and pyrite sulphur (according to PN-G-04582:1997 standard), organic sulphur, and total sulphur (according to PN-G-04584:2001 standard), caking power by Roga test (according to PN-81/G-04518 standard), and coal swelling index (according to PN-ISO501:2007 standard). The content of major element oxides was determined using a selective X-ray fluorescence spectrometer ZSX Primus II (detection limit in coal ash:  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3 = 0.5\%$ ;  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ , and  $\text{MgO} = 0.2\%$ ;  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{SO}_3$ , and  $\text{TiO}_2 = 0.1\%$ ;  $\text{P}_2\text{O}_5 = 0.05\%$ ) and the content of some trace elements (As, Ba, Co, Cr, Cu, Mn, Pb, Rb, Sr, V, Zn) in coal ash. The analysis included only those trace elements whose content in coal ash was greater than the limit of detection (detection limit of elements in coal ash: As = 6 ppm, Ba = 13 ppm, Co and Pb = 3 ppm, Cr and Mn = 6 ppm, Cu and Zn = 2 ppm, Rb = 7 ppm, Sr and V = 4 ppm). Standard conditions of analysis were kept: (Rh anode tube power=max. 4 kW, 50 kV/60 mA, and analytical crystals: PET, LiF1, Rx25, Ge). The content of trace elements in coal ash was recalculated into the content in coal. The standard deviation of the major elements content in coal ash ( $\text{SiO}_2 = 13.31\%$ ,  $\text{Al}_2\text{O}_3 = 7.87\%$ ,  $\text{Fe}_2\text{O}_3 = 8.47\%$ ,  $\text{CaO} = 6.88\%$ ,  $\text{MgO} = 2.58\%$ ,  $\text{Na}_2\text{O} = 1.04\%$ ,  $\text{K}_2\text{O} = 0.93\%$ ,  $\text{SO}_3 = 7.95\%$ ,  $\text{TiO}_2 = 0.38\%$ , and  $\text{P}_2\text{O}_5 = 0.78\%$ ) and the trace elements content in coal (As = 4.7 ppm, Ba = 153.4 ppm, Co = 6.9 ppm, Cr = 8.0 ppm, Cu = 11.8 ppm, Mn = 107.2 ppm, Pb = 18.7 ppm, Rb = 17.5 ppm, Sr = 110.7 ppm, V = 23.4 ppm, and Zn = 133.3 ppm) were calculated.

The mode of the occurrence of elements in coal was determined by two methods.

- The concentration distribution (CD) function of Marczak (1985) was used, as presented below:

$$CD = C_A = C_o \frac{A-1}{A} + KA + C_m$$

where:  $A$  – ash content expressed as a mass fraction,  $C_A$  – trace element concentration (g/Mg) in ash,  $C_o$  – average trace-element concentration (g/Mg) in organic coal substance,  $K$  – proportionality factor expressing a concentration increase (g/Mg) in ash,  $C_m$  – trace element concentration (g/Mg) in coal ash for a limit value  $A = 0$ .

Value  $A$  is determined empirically as the ash content in coal. The values of  $C_o$ ,  $K$  and  $C_m$  are determined mathematically by solving a system of three equations with three variables. ' $C_o(1 - A)/A$ ' in the above equation determines the part of the content of an element in coal ash that is associated with organic matter. ' $KA + C_m$ ' involves the part which results from the presence of an element in mineral matter. It has been previously shown that the CD function is useful in determining which part of a given trace-element concentration is associated with the organic fraction in coal, and which with the inorganic fraction (i.a.: Lewińska-Preis et al. 2009, Parzentny and Róg 2019). The results obtained are shown in Figure 1.

- Pearson's correlation coefficient values were calculated in order to find relationships between coal quality indices, the content of major element oxides in coal ash, and the content of trace elements in coal samples representing the coal seam. The hypothesis concerning the normal distribution of measurements was analysed using the Chi-square Pearson test, Kolmogorov-Smirnov test, and Shaphiro-Wilk test (with a significance level of  $\alpha = 0.05$ ). The linear regression determination coefficients  $R^2$  were determined for the relationships sought. The verification of the linear regression model was carried out using the F-Snedecor test, and the significance of the correlation coefficient  $r$  for the significance level of  $\alpha = 0.05$  was verified using the t-Student test. In the interpreta-

tion of  $r$  and  $p$  values, it was assumed that  $r \geq 0.35$  for  $p < 0.05$  indicate the significance of the correlation relationship studied. On the other hand, the values of  $r \geq 0.35$  for  $p = 0.05-0.20$  only suggest that the statistical analysis did not prove the significance of the correlation. At the same time, the absence of a significant correlation will not necessarily mean that particular parameters are not related. A significant correlation between two parameters may result from the relation with another factor. It is assumed that in the case of a wider range of values of the analysed parameters and an increased number of samples representing a coal seam the examined relationships would probably be significant. The Pearson correlation coefficient values were also calculated to find the relationship between the average values of the coal quality indices for coal seams, the average content of oxides in the main elements in coal ash, and the average content of trace elements in coal. These relationships can help find the reasons for the variability in the way elements occur in coal in the seam sequence from 209 to 620 in the USCB vertical profile. The results of the calculations are provided in Table 1.

Following the recommendations of Dai et al. (2020) the results obtained with statistical calculation methods (Fig. 1, Table 1 and 2) served to determine the organic and inorganic affinity of the analysed trace elements in the tested coal. Then they were used to conclude the probable role of groups of macerals and groups of minerals in concentrating elements in coal.

### 3. Results and discussion

#### 3.1. General coal characteristics

The petrographic composition of the studied coal from USCB calculated as coal without mineral matter (vitrinite = 63%, liptinite = 8%, inertinite = 29%; calculated on the basis of the data given in the signature of Fig. 1) is similar to the petrographic composition of Europe's Paleozoic coals in the North Atlantic macroregion (according to Vasconcelos (1999): vitrinite = 68%, liptinite = 12% and inertinite 20%). The content of mineral matter in coal is low (6.2%). The greatest components of the mineral matter are carbonate (2.2% in coal), sulfide (2.1%), clay minerals (1.5%), and quartz (0.4%); also trace amounts (<0.1%) of chalcopyrite, sphalerite and galena identified. Due to vitrinite random reflectance (0.77%), the studied coal is ortho-bituminous coal (according to the International Classification of Seam Coals, Final Version, 1998).

#### 3.2. Variability in the modes of the occurrence of elements in coal

Differentiation of the share of mineral and organic matter in the concentration of elements in coal was observed, in order from seam 209 to 620 (Fig. 1). These observations were supplemented by the interpretation of the Pearson correlation coefficient values given in Table 1. There was observed strong affinity of Ba, Co, Mn, Pb, Rb, Sr, V, and Zn to mineral matter in coal from seam 209 (Fig. 1a). However, differences were found in the role of the identified mineral groups in the concentration of some elements in coal. The data in Table 2 suggest that affinity of Mn to carbonate minerals and affinity of Pb to sulfide minerals. The presence of As, Cr and Cu in the coal of the analysed seam is determined by the amount of organic matter, mainly inertinite (this applies only to As and Cr).

TABLE 1

Pearson's correlation coefficient expressing the relationship between petrographic and physico-chemical indices of coal quality and the content of trace elements in coal from individual coal seams

		Coal seam									
	209	401	405	407	501	504	510	615	620		
	2	3	4	5	6	7	8	9	10		
As	I* = 0.97	S <sub>t</sub> <sup>a</sup> = 0.95	S <sub>t</sub> <sup>a</sup> = 0.64 (p = 0.09)		Cl = 0.66 (p = 0.15)	Cl = 0.91 (p = 0.09) Cb = 0.99 SiO <sub>2</sub> = 0.99 Al <sub>2</sub> O <sub>3</sub> = 0.99 TiO <sub>2</sub> = 0.97	S <sub>p</sub> <sup>a</sup> = 0.87	Na <sub>2</sub> O = 0.96	S <sub>s</sub> <sup>a</sup> = 0.82		
Ba	SO <sub>3</sub> = 0.95		Cl = 0.70 R <sub>r</sub> = 0.75 SiO <sub>2</sub> = 0.71 K <sub>2</sub> O = 0.83	Cl = 0.93 A = 0.99 K <sub>2</sub> O = 0.88	SiO <sub>2</sub> = 0.89 Al <sub>2</sub> O <sub>3</sub> = 0.84 K <sub>2</sub> O = 0.88 C <sup>daf</sup> = 0.96		Cl = 0.64 (p = 0.17) R <sub>r</sub> = 0.96	P <sub>2</sub> O <sub>5</sub> = 0.94 (p = 0.06) R <sub>r</sub> = 0.96			
Co		S <sub>s</sub> <sup>a</sup> = 0.97 I = 0.84 (p = 0.16)	MgO = 0.82	SiO <sub>2</sub> = 0.82 (p = 0.09) Al <sub>2</sub> O <sub>3</sub> = 0.87 (p = 0.55) P <sub>2</sub> O <sub>5</sub> = 0.84 (p = 0.07)	Cl = 0.94 Cb = 0.84 Sf = 0.94 SiO <sub>2</sub> = 0.87 K <sub>2</sub> O = 0.88	Vt = 0.89 (p = 0.11) Cl = 0.98 Cb = 0.95 (p = 0.05)					
Cr	I = 0.91 (p = 0.09)	Cl = 0.96 A <sup>a</sup> = 0.98	Al <sub>2</sub> O <sub>3</sub> = 0.68 (p = 0.07)	K <sub>2</sub> O = 0.96 Rr = 0.98	P <sub>2</sub> O <sub>5</sub> = 0.96	Vt = 0.95 Cl = 0.95	A <sup>a</sup> = 0.85 TiO <sub>2</sub> = 0.84				
Cu	C <sup>daf</sup> = 0.97	Vt = 0.90 (p = 0.09) Al <sub>2</sub> O <sub>3</sub> = 0.95	Al <sub>2</sub> O <sub>3</sub> = 0.67 (p = 0.07)		Cb = 0.67 (p = 0.15) Al <sub>2</sub> O <sub>3</sub> = 0.76 (p = 0.08)	Vt = 0.99 Cl = 0.98	A = 0.86 TiO <sub>2</sub> = 0.88	C <sup>daf</sup> = 0.97			

TABLE 1. Continued

1	2	3	4	5	6	7	8	9	10
Mn	Cb = 0.99	Cb = 0.89	CaO = 0.62	Rr = -0.96	Cl = 0.77	S <sub>p</sub> <sup>a</sup> = 0.99	Cl = 0.76	CaO = 0.98	
	CaO = 0.99	(p = 0.11)	(p = 0.10)		(p = 0.08)		(p = 0.08)	S <sub>s</sub> <sup>a</sup> = 0.97	
	MgO = 0.99	Fe <sub>2</sub> O <sub>3</sub> = 0.94					A = 0.85	Rr = -0.97	
Pb	S <sub>p</sub> <sup>a</sup> = 0.94	SiO <sub>2</sub> = 0.96		SiO <sub>2</sub> = 0.96	Cb = 0.82	Cb = 0.99	S <sub>p</sub> <sup>a</sup> = 0.84		
	(p = 0.63)	S <sub>p</sub> <sup>a</sup> = 0.97		Al <sub>2</sub> O <sub>3</sub> = 0.90	Sf = 0.79	SiO <sub>2</sub> = 0.99			
				TiO <sub>2</sub> = 0.96	(p = 0.06)	Al <sub>2</sub> O <sub>3</sub> = 0.99			
Rb	SO <sub>3</sub> = 0.90		Cl = 0.90	Cl = 0.99	Cl = 0.98	Vt = 0.97	A <sup>a</sup> = 0.83	Cl = 0.99	SiO <sub>2</sub> = 0.92
	(p = 0.09)		Q = 0.96	K <sub>2</sub> O = 0.95	P <sub>2</sub> O <sub>5</sub> = 0.98	Cl = 0.99	SiO <sub>2</sub> = 0.97	K <sub>2</sub> O = 0.96	Al <sub>2</sub> O <sub>3</sub> = 0.95
			A <sup>a</sup> = 0.96	A <sup>a</sup> = 0.98	C <sup>daf</sup> = 0.84	S <sub>o</sub> <sup>a</sup> = 0.98	Al <sub>2</sub> O <sub>3</sub> = 0.90	TiO <sub>2</sub> = 0.97	K <sub>2</sub> O = 0.97
Sr	Ti = 0.97	A <sup>a</sup> = 0.96	Cl = 0.83		Vt = 0.66		A <sup>a</sup> = 0.94	Al <sub>2</sub> O <sub>3</sub> = 0.96	
		S <sub>o</sub> <sup>a</sup> = 0.96	Q = 0.90		(p = 0.15)		SiO <sub>2</sub> = 0.81	K <sub>2</sub> O = 0.97	
			A <sup>a</sup> = 0.94		Cl = 0.89		Al <sub>2</sub> O <sub>3</sub> = 0.92	TiO <sub>2</sub> = 0.97	
V		SiO <sub>2</sub> = 0.77	SiO <sub>2</sub> = 0.77		P <sub>2</sub> O <sub>5</sub> = 0.98		TiO <sub>2</sub> = 0.96		
		K <sub>2</sub> O = 0.90	K <sub>2</sub> O = 0.90		C <sup>daf</sup> = 0.94				
		Sf = 0.92	Sf = 0.75	MM = 0.83	Cl = 0.95	Cl = 0.95	Vt = 0.96	A <sup>a</sup> = 0.99	SiO <sub>2</sub> = 0.91
Zn	S <sub>t</sub> <sup>a</sup> = 0.96	(p = 0.08)	A <sup>a</sup> = 0.87	(p = 0.08)	Cb = 0.97	Cl = 0.94	SiO <sub>2</sub> = 0.83		S <sub>s</sub> <sup>a</sup> = 0.82
		A <sup>a</sup> = 0.93	SiO <sub>2</sub> = 0.88	K <sub>2</sub> O = 0.93	Sf = 0.98	(p = 0.06)	Al <sub>2</sub> O <sub>3</sub> = 0.91		
		(p = 0.07)	Al <sub>2</sub> O <sub>3</sub> = 0.85		P <sub>2</sub> O <sub>5</sub> = 0.99	A <sup>a</sup> = 0.97	TiO <sub>2</sub> = 0.99		
	Cl = 0.88	Cl = 0.88	K <sub>2</sub> O = 0.82		C <sup>daf</sup> = 0.85	S <sub>o</sub> <sup>a</sup> = 0.96			
	(p = 0.12)	(p = 0.12)	TiO <sub>2</sub> = 0.80						
		S <sub>t</sub> <sup>a</sup> = 0.97	L = 0.51			Na <sub>2</sub> O = 0.97			
			(p = 0.19)						

\* Indicator symbols: V<sub>t</sub> – vitrinite, L – liptinite, I – inertinite, MM – mineral matter, Cl – clay minerals, Cb – carbonate minerals, Q – quartz, Sf – sulfide minerals (mainly pyrite > marcasite and <0.1% chalcopyrite+sphalerite+galena), R<sub>r</sub> – vitrinite reflectance, A<sup>a</sup> – ash yield, S<sub>s</sub><sup>a</sup> – sulphate sulphur, S<sub>p</sub><sup>a</sup> – pyritic sulphur, S<sub>o</sub><sup>a</sup> – organic sulphur, S<sub>t</sub><sup>a</sup> – total sulphur, C<sup>daf</sup> – carbon, RI – (Roga Index) coking strength, SI – swelling index

TABLE 2

Pearson's correlation coefficient expressing the relationship between petrographic and physico-chemical indices of coal quality and the content of trace elements in coal in the vertical USCB profile

As	Ba	Co	Cr	Cu	Mn	Pb	Rb	Sr	V	Zn
Cb* = 0.65 (p = 0.06)	Q = 0.84	MM = 0.63 (p = 0.07)	Cl = 0.61 (p = 0.08)		MM = 0.65 (p = 0.06)	MM = 0.70	Cl = 0.80	Q = 0.68	MM = 0.59 (p = 0.09)	
A <sup>a</sup> = 0.77	SiO <sub>2</sub> = 0.91	(p = 0.07)	(p = 0.08)		Sf = 0.92	Cb = 0.68	Q = 0.81	SiO <sub>2</sub> = 0.91	Cl = 0.63	
C <sup>daf</sup> = -0.63	Al <sub>2</sub> O <sub>3</sub> = 0.80	A <sup>a</sup> = 0.71	Q = 0.65 (p = 0.06)		Rr = -0.64	Sf = 0.73	A <sup>a</sup> = 0.68	Al <sub>2</sub> O <sub>3</sub> = 0.83	(p = 0.08)	
(p = 0.07)	K <sub>2</sub> O = 0.89		SiO <sub>2</sub> = 0.65 (p = 0.06)		(p = 0.06)	Rr = -0.72	SiO <sub>2</sub> = 0.77	K <sub>2</sub> O = 0.88	Q = 0.63	
	TiO <sub>2</sub> = 0.65 (p = 0.06)				S <sub>p</sub> <sup>a</sup> = 0.77	S <sub>s</sub> <sup>a</sup> = 0.80	K <sub>2</sub> O = 0.79	TiO <sub>2</sub> = 0.62	(p = 0.07)	
	RI = 0.81				S <sub>i</sub> <sup>a</sup> = 0.71	S <sub>p</sub> <sup>a</sup> = 0.89		(p = 0.08)	A <sup>a</sup> = 0.79	
					SI = -0.67	S <sub>i</sub> <sup>daf</sup> = -0.87		P <sub>2</sub> O <sub>5</sub> = 0.66 (p = 0.05)	SiO <sub>2</sub> = 0.82 K <sub>2</sub> O = 0.77	
						SI = -0.72		RI = 0.81		

\* Explanations as in Table 1



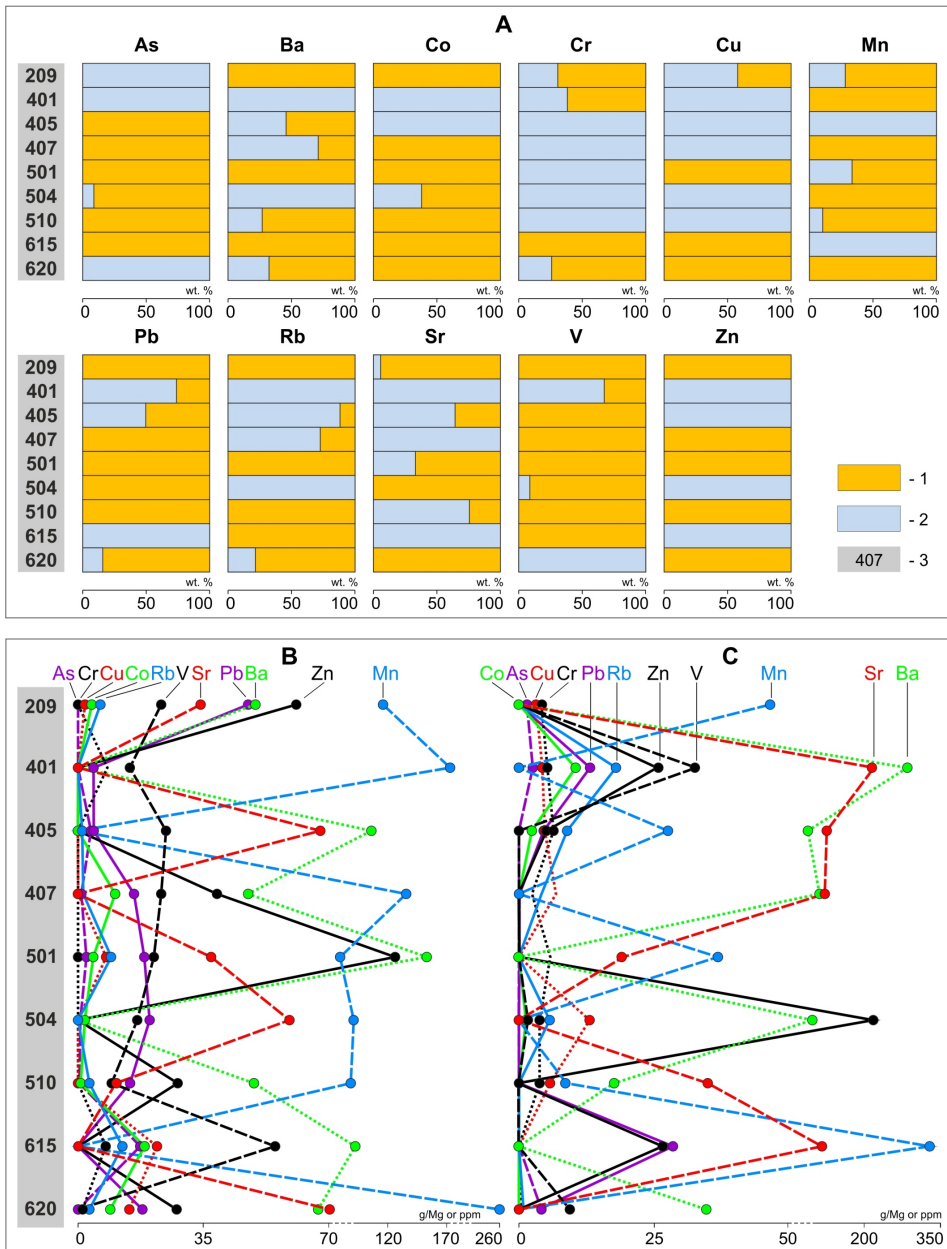


Fig. 1. Share (wt.%) of mineral and organic matter in the concentration of elements in coal (A\*), as well as the content of elements in mineral (B) and organic (C) matter of coal in the vertical USCBA profile; 1 – mineral matter (average content in the tested coal = 6.2%), 2 – organic matter (average content in the tested coal: vitrinite = 58.8%, liptinite = 7.6%, inertinite = 27.4%), 3 – coal seam symbol (\* the convergence of changes in the way elements occur in coal in the vertical USCBA profile, expressed using Pearson correlation coefficient, is  $r_{As-V} = 0.74$ ,  $r_{Ba-Rb} = 0.92$ ,  $r_{Co-Pb} = 0.60$ ,  $r_{Co-Zn} = 0.68$ ,  $r_{Mn-Pb} = 0.70$ ,  $r_{Pb-Zn} = 0.67$ ,  $r_{Co-Rb} = 0.74$  and  $r_{Cr-Cu} = 0.58$ ).

Mineral matter (Fig. 1a), and in particular clay minerals (only Cr) and carbonate (Mn) (Tab. 1) have a decisive role in the concentration of Cr and Mn in coal from seam 401. There is affinity of As, Ba, Co, Cu, Pb, Rb, Sr, V, and Zn to organic matter in coal (Fig. 1a). At the same time, the content of Co in coal is probably determined by the amount of inertinite and the content of Cu in coal by the amount of vitrinite, the content of As, Pb, V, and Zn in coal is probably determined (apart organic matter) by the amount of sulfide and/or sulphate minerals, and the content of V in coal of this seam is also probably determined by the amount of clay minerals (Tab. 1).

The content of As and V in coal from seam 405 is probably determined by mineral matter (Fig. 1a), especially clay and sulphide minerals (applies only to V; Tab. 1). There is affinity of Ba, Pb and Sr to mineral matter (probably mainly clay minerals: this refers to Ba and Sr) and organic matter (Fig. 1a, Tab. 1). In turn, is affinity of Co, Cr, Cu, Mn, Rb, and Zn to organic matter in coal (Fig. 1a). Additionally, the content of Co in coal may be determined probably by substances rich in magnesium. The content of Cr and Cu in coal can be determined probably by the content of substances rich in aluminium. The content of Mn in coal is probably determined probably by the amount of calcium-rich substances, the content of Zn in coal is determined probably by the amount of liptinite while Rb content in coal is determined (apart from organic matter) probably by the amount of clay minerals (Tab. 1).

There was observed affinity of As, Co, Mn, Pb, V, and Zn to mineral matter in coal from seam 407 (Fig. 1a). At the same time, clay and phosphate minerals probably decide on the Co content in coal, and clay minerals on the Pb content in coal (Tab.1). Organic matter plays an probably important role in the concentration of Ba, Cr, Cu, Rb, and Sr in the coal of this deposit (Fig. 1a). Furthermore, clay minerals are probably decisive in the content of Ba and Rb (apart from organic matter).

Mineral matter (Fig. 1a), and mainly clay minerals (applies to As, Ba, Co, Mn, Rb, Sr, V), carbonate (Co, Cu, Pb, V), sulfide (Co, Pb, V) and probably phosphate (V) and secondary vitrinite (only Sr) (Tab. 1) are of fundamental importance in concentrating As, Ba, Co, Cu, Mn, Pb, Rb, Sr, V, and Zn in coal from seam 501. In turn, the organic matter and possibly clay minerals probably decide on the Cr content in the coal from this seam.

Mineral matter plays an probably important role in concentrating As, Co, Mn, Pb, Sr, and V in coal from seam 504 (Fig. 1a). Additionally, clay and carbonate minerals probably determine the content of As, Co, and Pb in coal. In addition to mineral matter, the amount of vitrinite is also decisive in the content of Co in coal. Mn content in coal is probably determined by sulphide minerals, and the content of V in the coal of the analysed seam is determined by clay and vitrinite (Tab. 1). There is also strong affinity of Ba, Cr, Cu, Rb, and Zn to organic matter in coal from seam 504 (Fig. 1a). At the same time, vitrinite and clay minerals (this refers to Cu and Rb) probably determine the content of Cr, Cu, and Rb in coal, and the content of Zn in coal is probably determined by sodium rich substances (Tab. 1).

Mineral matter is probably decisive in the concentrating of As, Ba, Co, Mn, Pb, Rb, V, and Zn in coal from seam 510 (Fig. 1a). However, the content of As and Pb in coal is probably determined by sulphide minerals, and the content of Ba, Mn, and Rb in coal – by clay minerals (Tab. 1). There is also strong affinity of Cr, Cu, and Sr to organic matter, clay mineral inclusions (only Sr) and titanium-rich substances in the coal in question.

The content of As, Ba, Co, Cr, Cu, Rb, and V in coal from seam 615 is probably determined by mineral matter (Fig. 1a). Additionally, the content of As in coal is determined by sodium-rich phases, the content of Ba in coal is probably determined by phosphate minerals, and the content

of Rb in coal is probably determined by clay minerals (Tab. 1). Organic matter is probably important in the concentration of Mn, Pb, and Zn in coal from seam 615.

There was observed affinity of Ba, Co, Cr, Cu, Mn, Pb, Rb, Sr, and Zn to mineral matter in coal from seam 620 (Fig. 1a). There is also affinity of Rb to clay minerals, and affinity of As and V to organic matter in this coal (Tab. 1).

There are also trends in the content of elements in the mineral and organic matter of coal in the vertical profile of the USCB (Figs. 1b and 1c). In the mineral matter of coal from seam 209, the Pb content is highest in the USCB profile. The mineral matter of coal from seam 401 contains the most Cr and Mn, the mineral matter of coal from seam 405 contains the most Sr, the mineral matter of coal from seam 501 contains the most Ba and Zn, the mineral matter of coal from seam 615 contains the most As, Co, Cr, Cu, Rb, and V, and the mineral matter of coal from deposit 620 has the highest Mn content (Fig. 1b). In the mineral matter of coal from seams 407, 504 and 510 and in the organic matter of coal from seams 209, 405, 407, 501, 510, and 620 there are no elevated contents of elements (Figs. 1b and 1c). However, it was observed that the organic matter of coal from seam 401 has the most Ba, Co, Rb, Sr, and V. The organic matter of coal from seam 504 has the most Cu and Zn, and the organic matter of coal from seam 615 has the highest content of Mn and Pb (Fig. 1c).

The above analysis of the data shows the existence of differences in the probably way elements occur in coal not only between but also within coal basin and seams (as previously stated by, among others, Finkelman et al. 2018, Yudovich and Ketris 2005) and between lithostratigraphical members (e.g. Parzenty 1994, Parzenty and Lewińska 2006, Chen et al. 2017), but also between coal seams. The observations presented in this paper are important for the selection of clean coal preparation procedures, i.e. free from elements which are potentially dangerous to the environment, and for forecasting the content of elements in coal combustion products. The aforementioned strong affinity of As to organic matter in coal from seam 209, affinity of As, Ba, Co, Cu, Pb, Rb, Sr, V, and Zn to organic matter in coal seam 401, affinity of Co, Cr, Cu, Mn, Rb, and Zn to organic matter in coal from the 405 seam, affinity of Ba, Cr, Cu, Rb, and Sr to organic matter in coal from seam 407, affinity of Cr to organic matter in coal from seam 501, affinity of Ba, Cr, Cu, Rb, and Zn to organic matter in coal from seam 504, affinity of Cr, Cu, and Sr to organic matter in coal from seam 510, affinity of Mn, Pb, Sr, and Zn to organic matter in coal from seam 615, and affinity of As and V to organic matter in coal from seam 620 was assessed as unfavourable for clean fuel preparation process energy. However, the probably large or exclusive effect of sulfide and/or carbonate minerals on the Mn and Pb content in coal from seams 209 and 401 (applies only to Mn), on the V content in coal from seam 405, on the content of Ba, Co, Cu, Pb, Rb, Sr, and V in coal from seam 501, for the content of As, Co, Mn, and Pb in coal from seam 504, on the content of As and Pb in coal from seam 510 was considered beneficial for the possible purification of coal from these elements. Removal of elements from macerals and the removal of sub microscopic inclusions of native minerals of these elements from coal by means of gravity separation and flotation is generally considered ineffective (e.g. Chen et al. 2017, Duan et al. 2018). In turn, chalcophilic elements found in epigenetic grains of sulphides of > 50 µm in size can be removed from coal using satisfactory efficiency (<80%) by means of gravitational purification and/or flotation (e.g. Liu et al., 2019; Mohanty et al., 1998; Parzenty, 1995).

There are fears of burning the tested coal, with a high content of ecotoxic elements in organic matter of coal and coal in which these elements are associated with sulphides (Fig. 1c). It is assumed that the elements bound in coal in this way first evaporate and then are easily adsorbed in the fine particles of fly ash. The opposite is true for elements combined with other minerals,

as they probably remain in the ash matrix or slowly evaporate (Hower et al., 2016; Sekine et al., 2008; Xu et al., 2003; Zhao et al., 2018). It is best to avoid extracting coal from coal deposits rich in ecotoxic elements and to avoid burning such coal (just like it was done in the USA; Finkelman, 2007) or use effective and economically beneficial methods of coal purification (i.a. Makowska et al., 2016; Wierońska et al., 2017).

The same or a similar mode of occurrence for two or three elements is noteworthy, as is the tendency to change the content of elements in the mineral and organic coal in the USCB profile (see Pearson correlation coefficient  $r$  in Fig. 1). This tendency was observed for As and V, Ba and Rb, Co and Pb, Co and Zn, Mn and Pb, Pb and Zn, Co and Rb and for Cr and Cu. There was no correlation between the changes in the way Sr occurs with other elements in coal in the USCB profile. The interdependencies found concerning the way elements occur in coal probably result from their common chemical affinity for oxygen, sulphur and iron. The co-occurrence of Co and Rb as well as Cr and Cu is difficult to explain based on their chemical affinity. However, it is possible for these elements to coexist in independent ingrown or fused phases with minerals that do not usually contain these elements but are often found in coal. Numerous sulfide nanoparticles and sulphosalts containing, among others, Co, Cu, Ni, Pb and Zn with a size of 5 nm-100 nm have been identified in the hydrothermal pyrite (Bielowicz & Misiak, 2017; Deditius et al., 2011; Parzenty, 1995). The substitution of elements which replace iron probably plays a key role in the accumulation of Cd, Ni, Pb and Zn in disulfides. This diadochy has already been described in bituminous coal deposits (Jiang et al., 2016; Kolker, 2012). However, Cr admixtures in disulfides may originate from the inclusion of clay minerals, mainly illite, previously observed in Pennsylvanian Coal in the Adaohai Mine, Daqingshan Coalfield in China (Dai et al., 2003; Huggins et al., 2000).

It was found that changes in the values of some coal quality indices in coal seams coincide with changes in the content of some trace elements in coal seams in the direction from seam 209 to seam 620; this is visible from the significant values of the Pearson correlation coefficient (Tab. 2). It is believed that the changes in the mode of the occurrence of As and Pb in coal in the USCB profile are significantly associated by carbonate mineralization, changes in the manner of the occurrence of Mn and Pb in coal is probably determined by sulfide mineralization, and the content of Ba, Cr, Rb, Sr, and V in coal from these deposits is associated by the presence of clay minerals.. There is no data (Table 2) that could explain the reasons for the variability of the mode of occurrence of the Co, Cu and Zn in carbon in the USCB profile. The high impact of dia- and epigenetic sulfide and carbonate mineralization on the occurrence in the USCB of the increased content of chalcophilic elements has already been observed (Parzenty & Róg, 2018; Parzenty & Lewińska, 2006). The enrichment of coal with trace elements probably occurred in the period of time between Permian and Quaternary, due to the migration of teletermaline brines that contributed to the formation of Triassic Carbonate-Hosted Zinc-Lead Deposits in Upper Silesia (Górecka et al., 1996).

It was also observed that the higher the carbonization of organic matter (expressed by the value of Rr and the content of C in coal), the lower the content of As, Mn and Pb in coal and the higher the content of Ba and Sr in coal in some of the coal seams discussed (Tabs. 1 and 2). The described trend of changes in the content of elements was probably caused by the destruction of metal-organic compounds and the condensation of carbon atoms in the carbon macromolecule during carbonization (Zubović et al. 1964). The concentration of metal-organic compounds is higher in the low-carbon organic matter of peat and lignites than in bituminous coal (including Dai et al., 2020; Eskenazy, 1972). The low stability of the As, Mn, and Pb complex connections and excess sulphur ions in the carbon-forming environment, probably at the initial stage of

diagenesis, contributed to the crystallization of the sulphides identified in the examined coals (chalcopyrite, sphalerite, galena, see Tab. 2). The high stability of the metal-organic compounds Ba and Sr probably had an impact on the relatively high concentration of these elements in the tested bituminous coal. In addition, the content of Ba and Sr in coal could have been influenced by the epigenetic mineralization of sulphate minerals found in USCB coal seams (Niec & Łabuś, 1966).

## 4. Conclusions

1. By interpreting the calculated values of the Pearson correlation coefficient and calculations using the CD function, differentiation was observed between the share of mineral and organic matter in the concentration of elements in coal, in order from seam 209 to seam 620, while stating differences in the role of identified groups of minerals and macerals in the concentration of certain elements in certain coal seams.
2. The same or a similar tendency of changes in the mode of occurrence of As and V, Ba and Rb, Co and Pb, Co and Zn, Mn and Pb, Pb and Zn, Co and Rb and for Cr and Cu in the coal seams in the USCB profile was found, probably due to their chemical affinity.
3. Changes in the method of occurrence of As and Pb in coal in the USCB profile were probably influenced by carbonate mineralization, the changes in the occurrence of Mn and Pb in coal were probably determined by diagenetic and epigenetic sulfide mineralization, and the content of Ba, Cr, Rb, Sr, and V in coal from these deposits was affected by clay minerals.
4. It was observed that the higher the carbonization degree of the organic matter of coal, the lower the content of As, Mn and Pb in coal, and the higher the content of Ba and Sr in coal.

It is believed that the above findings may be useful when making decisions about the qualification of coal from a coal seam for extraction, enrichment and combustion.

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