

Article

# Spatial Macroscale Variability of the Role of Mineral Matter in Concentrating Some Trace Elements in Bituminous Coal in a Coal Basin—A Case Study from the Upper Silesian Coal Basin in Poland

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Received: 17 April 2020; Accepted: 7 May 2020; Published: 9 May 2020



**Abstract:** As there are numerous claims that the mode of occurrence of trace elements in coal influences the quality of the substrates as well as the course and results of the coal preparation processes, it is necessary to analyse the differences in the mode of occurrence of the elements in coal within a coal basin or a coal deposit. With the use of concentration distribution functions and the Pearson correlation coefficient, it was concluded that (1) mineral matter plays a significant and nearly constant or constant role in concentrating V, Cr, Co, As, Rb, Sr, Ba, and Pb in coal; (2) organic matter plays a stable role in concentrating Sn; and (3) there are significant differences in the role of organic and mineral matter in concentrating Mn, Ni, Cu, Zn, Mo, Cd, and Sb in coal throughout the USCB (Upper Silesian Coal Basin). Moreover, there was observed a difference in the mode of occurrence of Cr, Mn, Co, Ni, Cu, Zn, Mo, Cd, Sn, and Sb in coal in the vertical profile of the USCB. At the same time, there were observed no differences and a stable significant role of mineral matter in concentrating V, As, Rb, Sr, Ba, and Pb in coal, while the role of the petrographic groups of the coal components in concentrating the elements in raw coal was differentiated. It is believed that the difference in the mode of occurrence of the trace elements in coal within coal seams and coal deposits is a geochemical regularity.

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

## 1. Introduction

Coal consists of organic and mineral matter; in turn, mineral matter consists of crystalline minerals, non-crystalline mineraloids, and elements with non-mineral associations [1,2]. In coal, elements are found in the organic and mineral compounds, as well as in the intimate organic associations; the latter including those adsorbed on to the surface of organics, dissolved in pore waters, and hosted in submicro- or nano-minerals, encased by the organic matter of coal [1]. The distribution of elements in a coal deposit is a result of the processes associated with the accumulation of organic matter carbonisation through the interaction between the organic matter, hydrothermal solutions, and volcanic interferences [1–5]. It is well known that coal is an invaluable paleoenvironmental, paleoclimatic, and geodynamic indicator of the deposition environment of organic matter. This was confirmed by the results of numerous studies of the botanical, geochemical, mineralogical, palynological, and petrological composition [3]. Recently, an important role of the new chronometric indicator of marine sediments and carbon age has been demonstrated; it is expressed by the ratio of strontium isotope content  $^{87}\text{Sr}/^{86}\text{Sr}$  and the presence of syngenetic gypsum in coal [6]. The mineral matter in coal also provides a range of useful information on the depositional conditions of coal-bearing sequences [4,5].

It is assumed that minerals are the hosts of the vast majority of elements present in coal [2]. The most trace elements and their highest content are found in sulphide, carbonate, and clay minerals [7–16].

The analyses of the content and the binding mode of the elements in coal are important, to know where and why they are concentrated in coal deposits; this would also provide more informed forecasts of the volume of elements released into the environment as a result of the combustion, weathering, and leaching of coal in deposits or storage yards [9,17–23]. The analyses also facilitate forecasting the effectiveness of various procedures of purifying coal of interlaying mineral matter and heavy metals [9,22,24–27]. Radioactive elements and heavy metals [5,28–30], referred to as ecotoxic elements by Duffus [31], are considered to be the most toxic for the environment. In turn, geochemical studies on the content and mode of occurrence of critical elements in coal and its combustion residues, especially rare earth elements, are of great importance for assessing the efficiency of their enrichment, extraction, and possible recovery [32–37].

The average content of trace elements in coal and general regularity of their binding mode in coal are generally known [2,5,10,23,38,39]. However, it is often observed that the parameters of coal differ between deposits, and may even differ within the lithostratigraphic parts of the deposit or a single coal seam. Variability of the geochemical parameters of coal probably influences the physical and chemical properties of the expected products and by-products of coal cleaning and processing and the scale of possible environmental contamination. The elements associated with organic matter evaporate and get condensed on the fine particles of the fly ash much easier than when they are related to, e.g., oxides and aluminosilicates—even if their melting temperature is high [17,23,40]. It is then necessary to analyse the range of changes in the role of organic matter and mineral matter in concentrating the trace elements within a coal deposit or a coal basin.

The article aims to 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 profile and the horizontal profile of a coal basin. The aim is achieved through analysing coal of the Upper Silesian Coal Basin (USCB), i.e., the biggest bituminous coal basin in Poland. This article is a continuation of the author's research on the modes of occurrence of trace elements in bituminous coal started in 1992. The results base collected in 2015 was already partly used for two publications. They are devoted to the search for interrelationships between the petrographic, geochemical, and physico-chemical indicators of coal quality in the Paralic Series [41], forms of mineral matter accumulations in coal, and the distribution of some trace elements in the mineral matter of coal seams in the Limnic Series of the USCB [42]. The need to continue the research undertaken in 1992 results from the supposition that there is still an undocumented range of variability in the way trace elements occur in lithostratigraphic and regional parts of the coal deposit or basin. This variability is probably of great importance for forecasting the use of new coal processing technologies and for environmental protection.

## 2. Geological Setting

The Upper Silesian Coal Basin (USCB) is located in southern Poland and in the Ostrava–Karviná region in the Czech Republic. This USCB comprises two coal-bearing series, i.e., the Paralic Series of Namurianian A and the Limnic Series from Namurianian B to Westphalian D (Figures 1 and 2). The geological structure, size of the coal deposits, and the coal parameters vary in the western, central, and eastern part of the USCB. In the western part of the USCB, the Carboniferous series is the thickest. It was subjected to intense folding and volcanism, and has most of the coal seams [43]. The coal itself shows significant differences in the degree of transformation of organic matter (expressed using coal reflectance  $R_r = 0.5\text{--}2.1$ ; [44]). The central part of the USCB shows relatively moderate differences in the number, thickness, inclination, and coal rank of the seams ( $R_r = 0.5\text{--}1.6$ ). The coal seams have low inclination and they form large troughs and anticlines. In the eastern part of the basin, the thickness of the Carboniferous series is significantly reduced, and the groups of seams join in the eastern part into thick seams (maximum 24 m); the degree of transformation of the organic matter in the coal is low

and shows relatively few differences ( $Rr = 0.5\text{--}0.7$ ). In the large area of Pennsylvanian rocks, there are located Triassic lime and dolomite rocks, where Zn–Pb deposits occur.

The geology of the USCB Pennsylvanian sequences has been described in detail by, e.g., Jureczka and Kotas [45] and Jureczka et al. [46]. The Zn–Pb deposits have been described in detail by, e.g., Górecka et al. [47].

### 3. Materials and Methods

The study included bituminous coal from 48 seams in 43 mines located in the USCB (Figures 1 and 2). A total of 111 samples were collected by cutting a column of coal from the roof to the floor of each seam. The coal samples were collected from the seams of nearly constant thickness and extent throughout the deposits.

The petrographic composition and coal reflectivity were determined using a Zeiss Axio Imager D1m microscope (Oberkochen, Germany, 40× objective, 10× oculars, and 546-nm interference filters, non-polarized reflected light, and oil immersion with the refractive index  $n = 1.5176$  at 23 °C) in accordance with the standards defined by the International Committee for Coal and Organic Petrology and the procedures described in ISO 7404-3 [48] and PN-ISO 7404-5 [49]. Ash yield was determined according to PN-ISO 1171:2002. [50] (see Supplementary Material, Table S1).

Wavelength Dispersive X-ray Fluorescence trace-element analyses were carried out using a ZSX Primus II spectrometer (Rigaku, Ettlingen, Germany, Rh anode tube power = max. 4 kW, 50 kV/60 mA, and analytical crystals: PET, LiF1, Rx25, Ge). Contents of the major elements in coal ash ( $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ , and  $\text{SO}_3$ ) and the content of V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Mo, Ag, Cd, Sn, Sb, Ba, and Pb were determined for the coal ash and converted to contents in coal based on the corresponding ash yield (see Table S1).

The hypothesis concerning the normal distribution of measurements was analysed using the Chi-square Pearson test, Kolmogorov–Smirnov test, and Shapiro–Wilk test (with a significance level of  $p = 0.05$ ). Then, the following was calculated:

- the arithmetic mean value of all the determined quality indices of the tested USCB coal and the average content of the oxides of the major elements in coal ash, which were compared with the average values of the coal indices of coal ranked from other deposits around the world (Table 1; see also Tables S1 and S2); and
- the average content of the elements in the coal, which were compared with hard coal Clarke values [38] (Table 1; see also Tables S1 and S2).

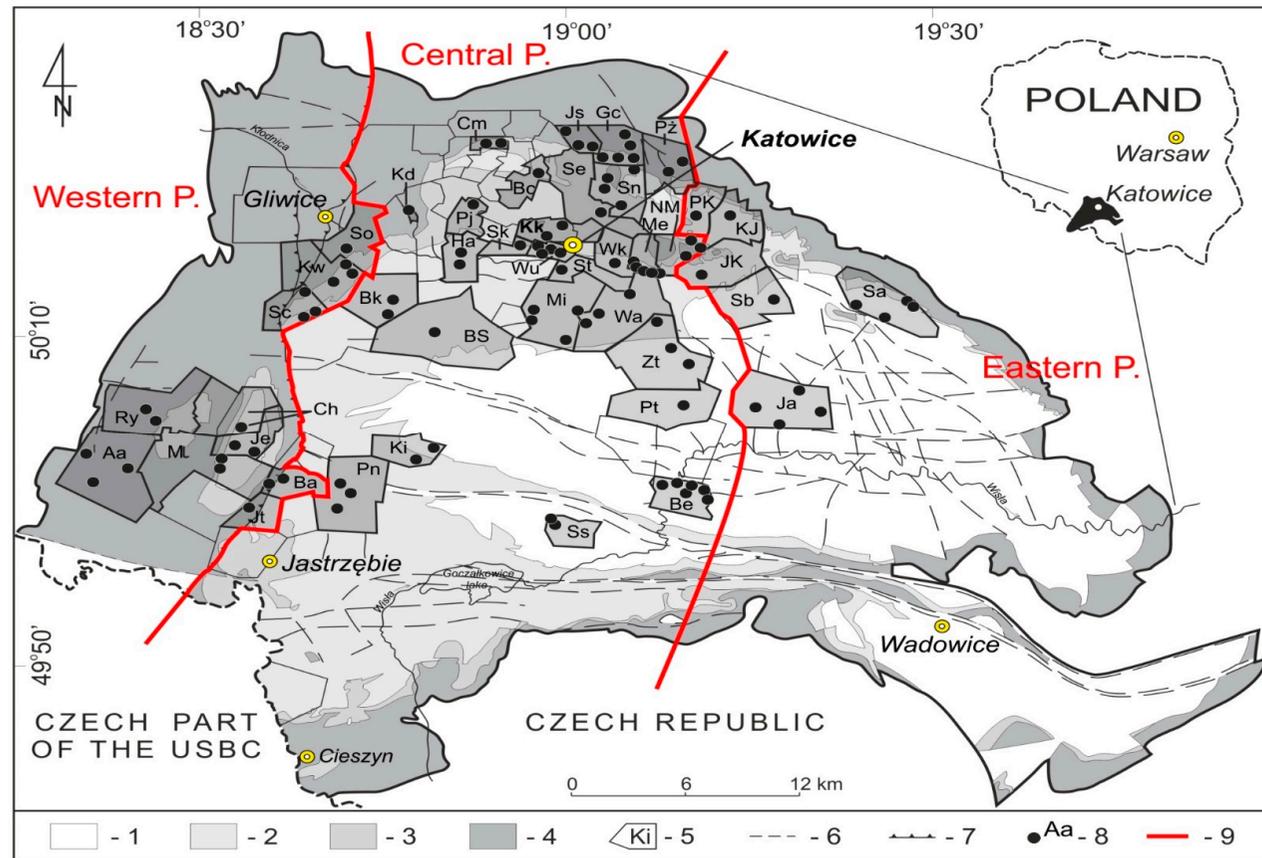
The mode of occurrence of the elements in coal was determined in two ways, i.e.:

- applying the function of the distribution of concentrations developed by Marczak [51], described with the following equation:

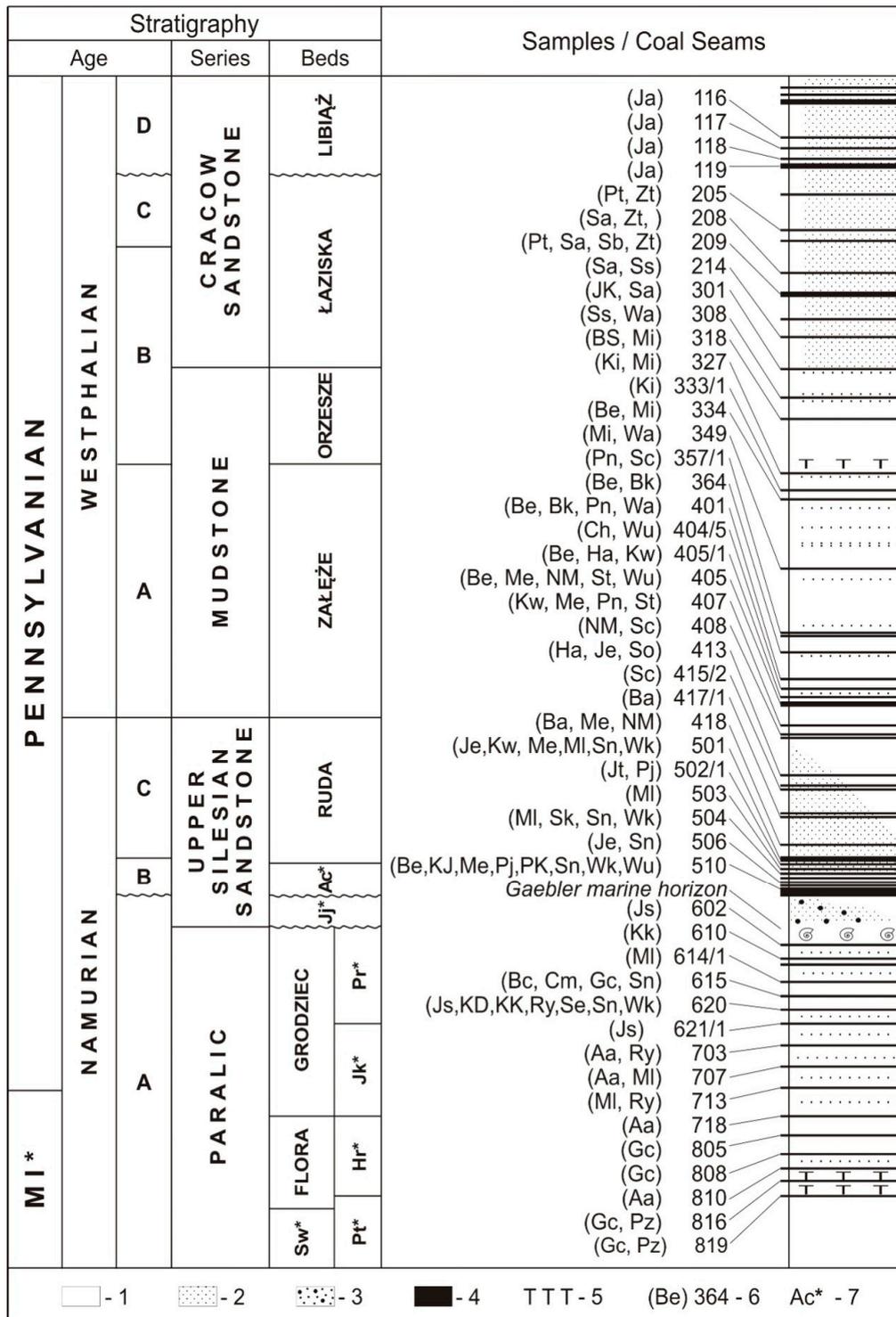
$$CD = C_A = C_o \frac{A-1}{A} + KA + C_m$$

where:

$A$ —ash yield expressed as a mass fraction;  $C_A$ —element concentration (g/Mg) in ash;  $C_o$ —average element concentration (g/Mg) in the organic coal substance;  $K$ —proportionality factor, expressing a concentration increase (g/Mg) in ash; and  $C_m$ —element concentration (g/Mg) in coal ash for a limit value  $A = 0$ .



**Figure 1.** Location of the sampling places in the Upper Silesian Coal Basin (USCB) (the geological structure according to Jureczka et al. [46]). 1—Cracov Sandstone Series; 2—Mudstone Series; 3—Upper Silesian Sandstone Series; 4—Paralic Series; 5—active and closed coal mines boundaries; 6—thrusts; 7—fault; 8—sampling places (Aa—Anna, Ba—Borynia, Bc—Barbara-Chorzów, Be—Brzeszcze, Bk—Budryk, BS—BolesławŚmiały, Ch—Chwałowice, Gc—Grodziec, Ha—Halemba, Ja—Janina, Je—Jankowice, JK—Jan Kanty, Js—Jowisz, Jt—Jastrzębie, Kd—Guido, KJ—Kazimierz-Juliusz, Ki—Krupiński, Kk—Katowice-Kleofas, Kw—Knurów, Me—Mysłowice, Mi—Murcki, Ml—Marcel, NM—Niwka-Modrzejów, Pj—Pokój, PK—Porąbka-Klimontów, Pn—Pniówek, Pt—Piast, Pz—Paryż, Ry—Rydułtowy,, Sa—Siersza, Sb—Sobieski, Sc—Szczygłowice, Sk—Śląsk, Sn—Saturn, So—Sośnica, Ss—Silesia, St—Staszic, Wa—Wesoła, Wk—Wieczorek, Wu—Wujek, Zt—Ziemowit); and 9—line dividing the USCB (after Kotas [43]) into the western, central, and eastern parts.



**Figure 2.** Lithostratigraphical profile of the USCB (from Jureczka et al. [46], with locations of samples shown). 1—mudstone; 2—sandstone; 3—conglomerate with sandstone; 4—coal; 5—tuffite; 6—coal seams with number and mine code (as in Figure 1); and 7—name abbreviation stratigraphic member: MI—Mississipian, Ac—Anticlinal, Jj—Jejkowice, Pr—Poruba, Jk—Jaklovec, Hr—Hrušov, Pt—Petřkovice, and Sw—Sarnów.

The value  $A$  is determined empirically as the ash content in the coal. 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 that part of the content of an element in the coal ash that is associated with organic matter. " $KA + C_m$ " involves the part that results from the presence of an element in the mineral matter. Solving the equation above enables calculating what part (expressed as wt.%) of the average content of the element in coal (g/Mg or ppm) originates from organic matter and mineral matter (see Table S3). It has been previously shown that the CD function is useful in determining the modes of occurrence of trace elements in coal (e.g., [52,53]). The results obtained are given in Figures 3 and 4 (see also Tables S4 and S5).

- Through calculating the value of the Pearson correlation coefficient ( $r$ ) for the dependence between the petrographic composition of coal, the content of the oxides of the main elements in coal ash, the content of sulphur in the coal and coal ash yield, and the content of the elements in the coal were determined. The coefficients of determination of the linear regression ( $R^2$ ) for the analysed dependencies were also determined. The linear regression model was verified with the F-Snedecor test with the level of confidence  $\alpha = 0.05$ . The significance of the correlation coefficient  $r$  for the significance level of  $p < 0.05$  was verified with a Student's t-test. Interpreting the values of  $r$  and  $p$ , it was assumed that the values  $r \geq 0.30$  for  $p < 0.05$  indicate the significance of the analysed correlation. The values  $r \geq 0.30$  for  $p = 0.05-0.10$  only enable a conclusion that the conducted statistical analysis did not provide any proof that the correlation is significant. The results of the calculations are presented in Tables 2 and 3 (see also Tables S6 and S7).

Following the recommendations of Dai et al. [1], the results obtained with the statistical calculation methods (Figures 3 and 4, as well as Tables 2 and 3) 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 the coal.

## 4. Results and Discussion

### 4.1. General Petrographical and Chemical Characteristics of Coal

The data presented in Table 1 show that, due to vitrinite random reflectance (0.74%), the tested USCB coal is orthobituminous (according to the International Classification of Seam Coals), and due to its ash yield average (11.60%) the tested coal is of medium purity [54]. The content of total sulphur in coal (1.16%) is medium-high, according to the criteria by Chou [55]. The petrographic composition of the coal is similar to the petrographic composition of the Palaeozoic coals in the North Atlantic (calculated on coal free of minerals) macroregion of Europe (see Vasconcelous [56]). The content of minerals in the coal is low (6.2%); of these, most are sulphide minerals (2.4%), clay minerals (1.9%), and carbonate minerals (1.8%). There was identified a trace amount of chalcopyrite, sphalerite, and galena (<0.1%).

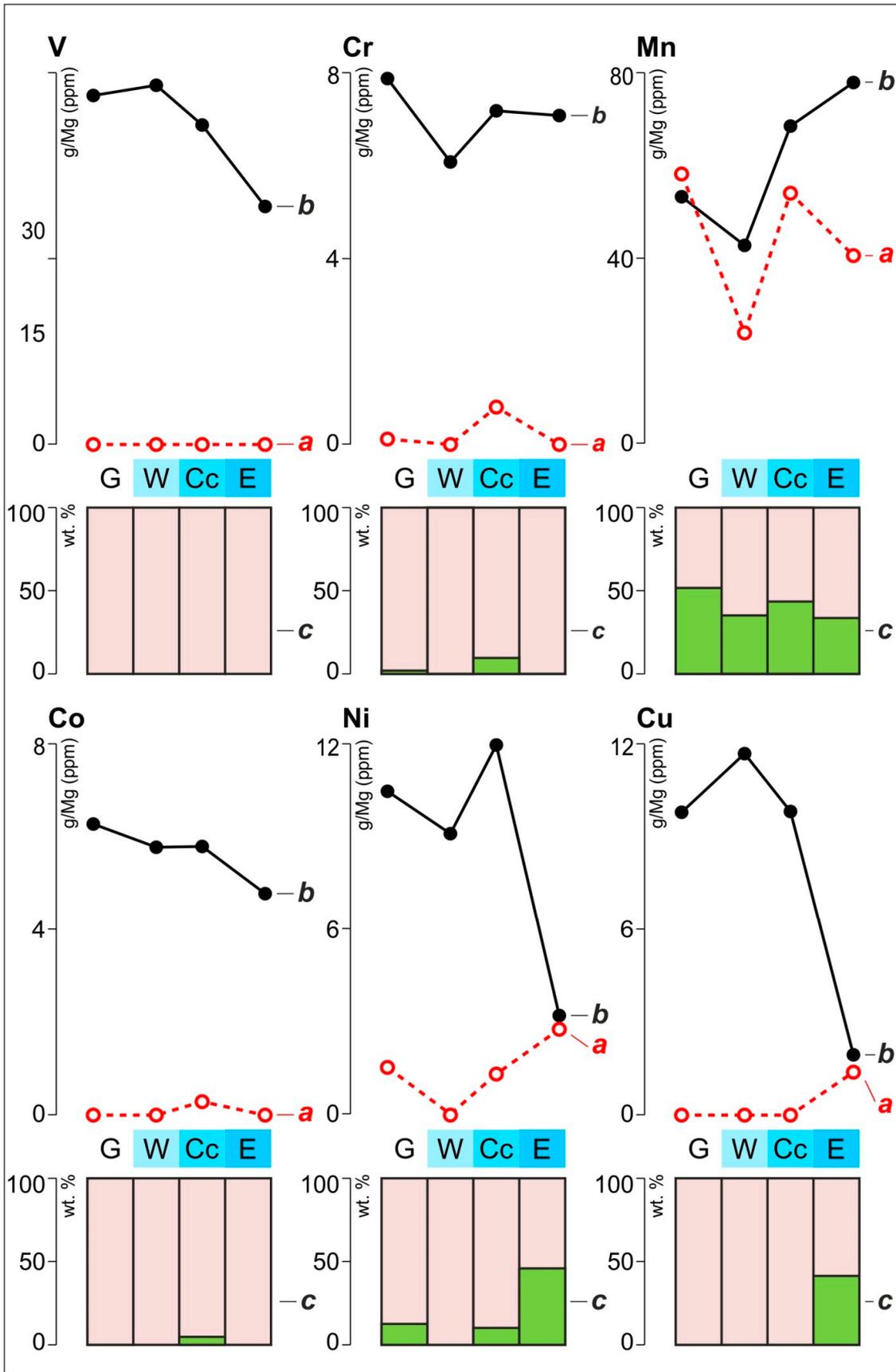


Figure 3. Cont.

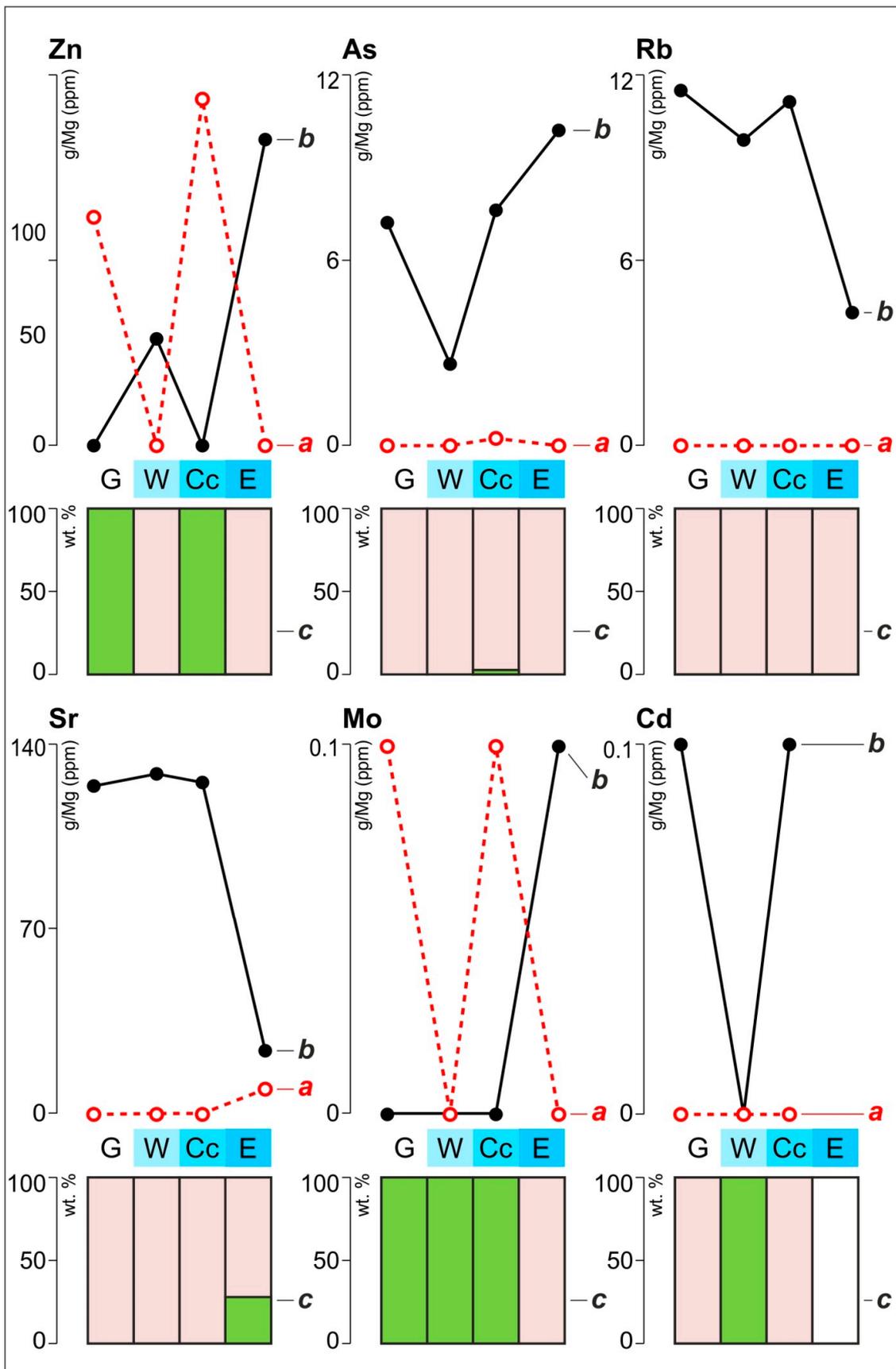
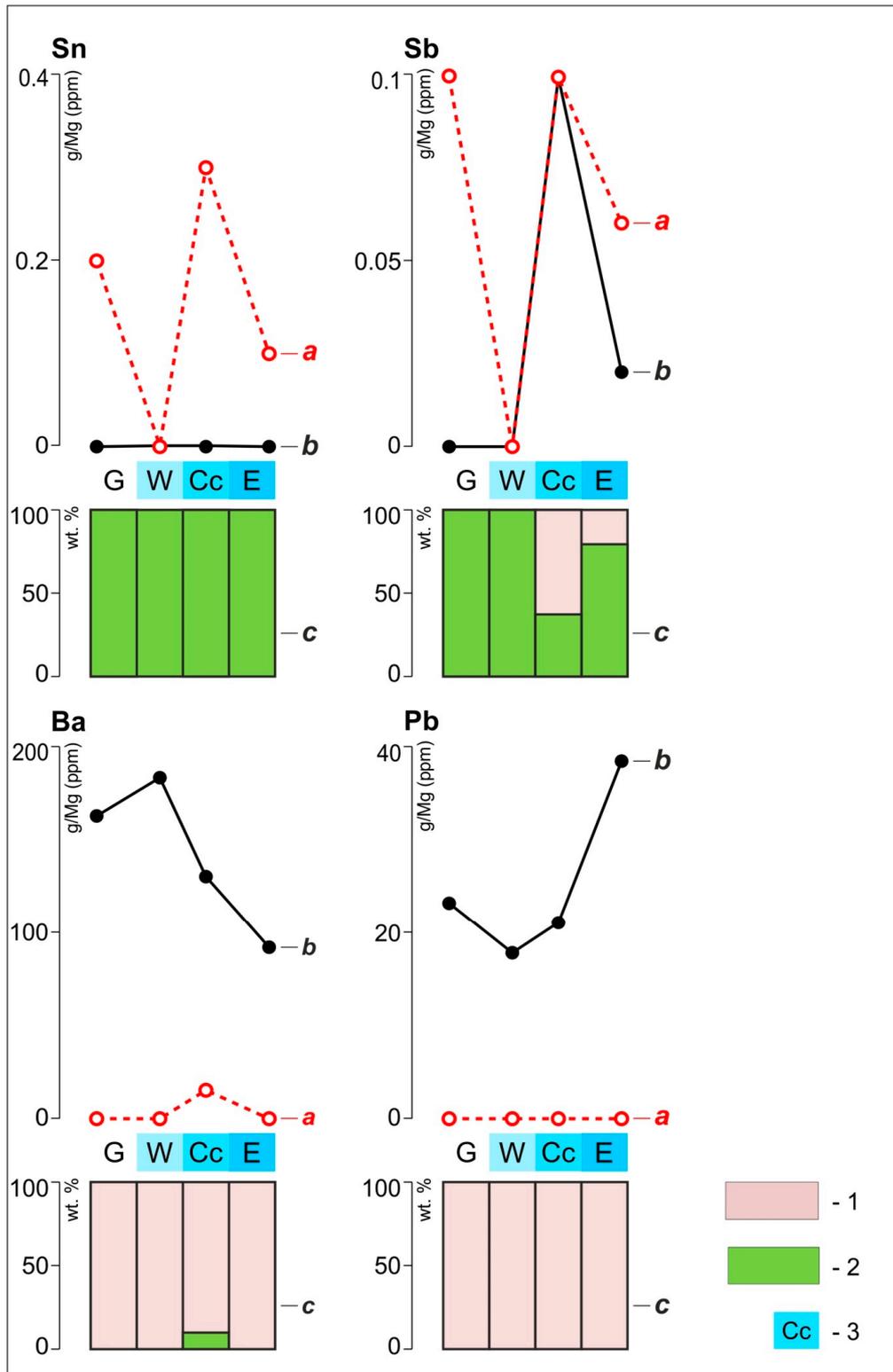


Figure 3. Cont.



**Figure 3.** The content of elements in the organic matter (a) and mineral matter (b) of the coal and the role of organic matter and mineral matter in concentrating the elements in the USCBA coal (c). 1—mineral matter; 2—organic matter; 3—parts of the USCBA: W—western, Cc—central, E—eastern, and G—generally the USCBA.

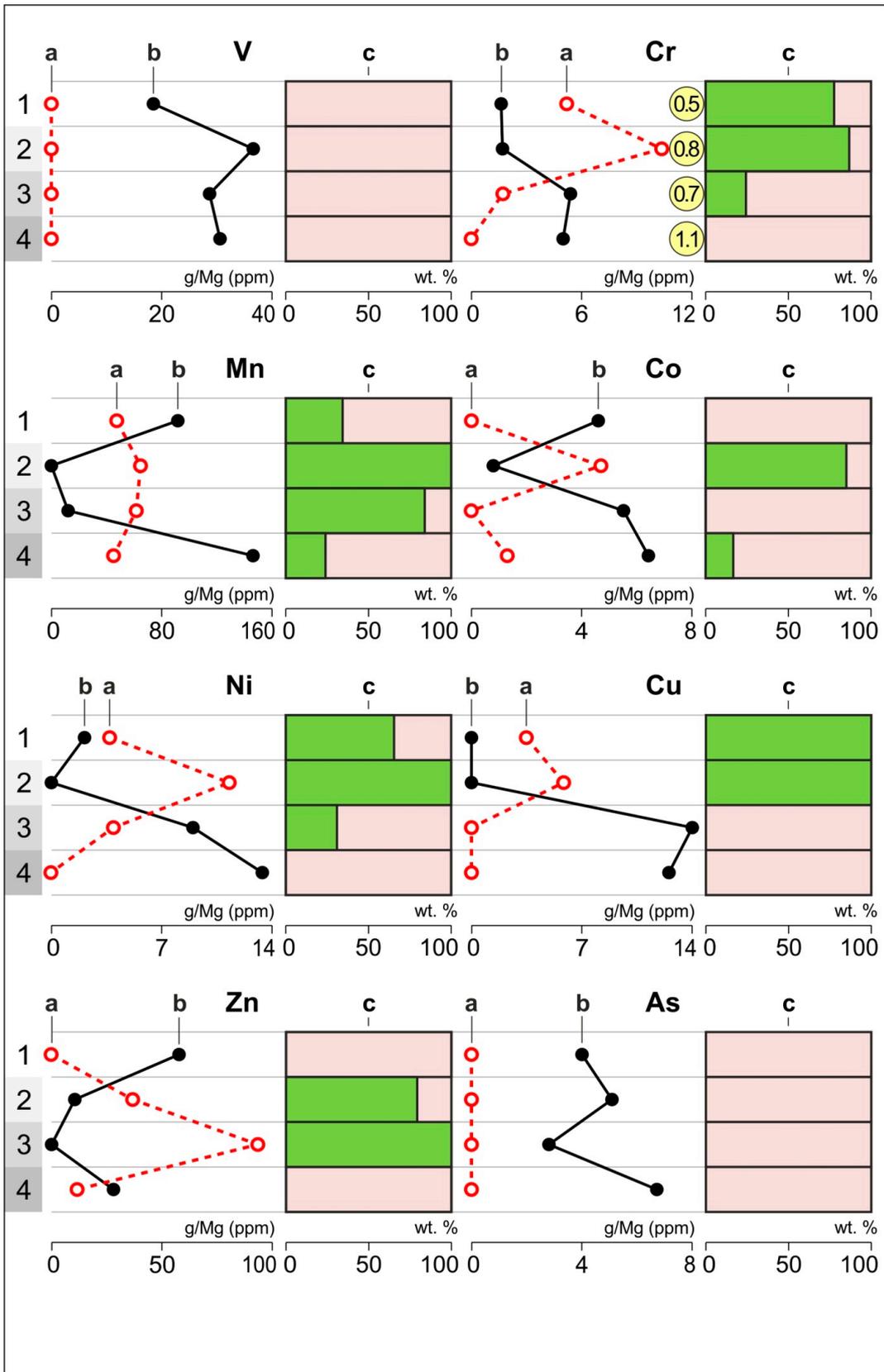
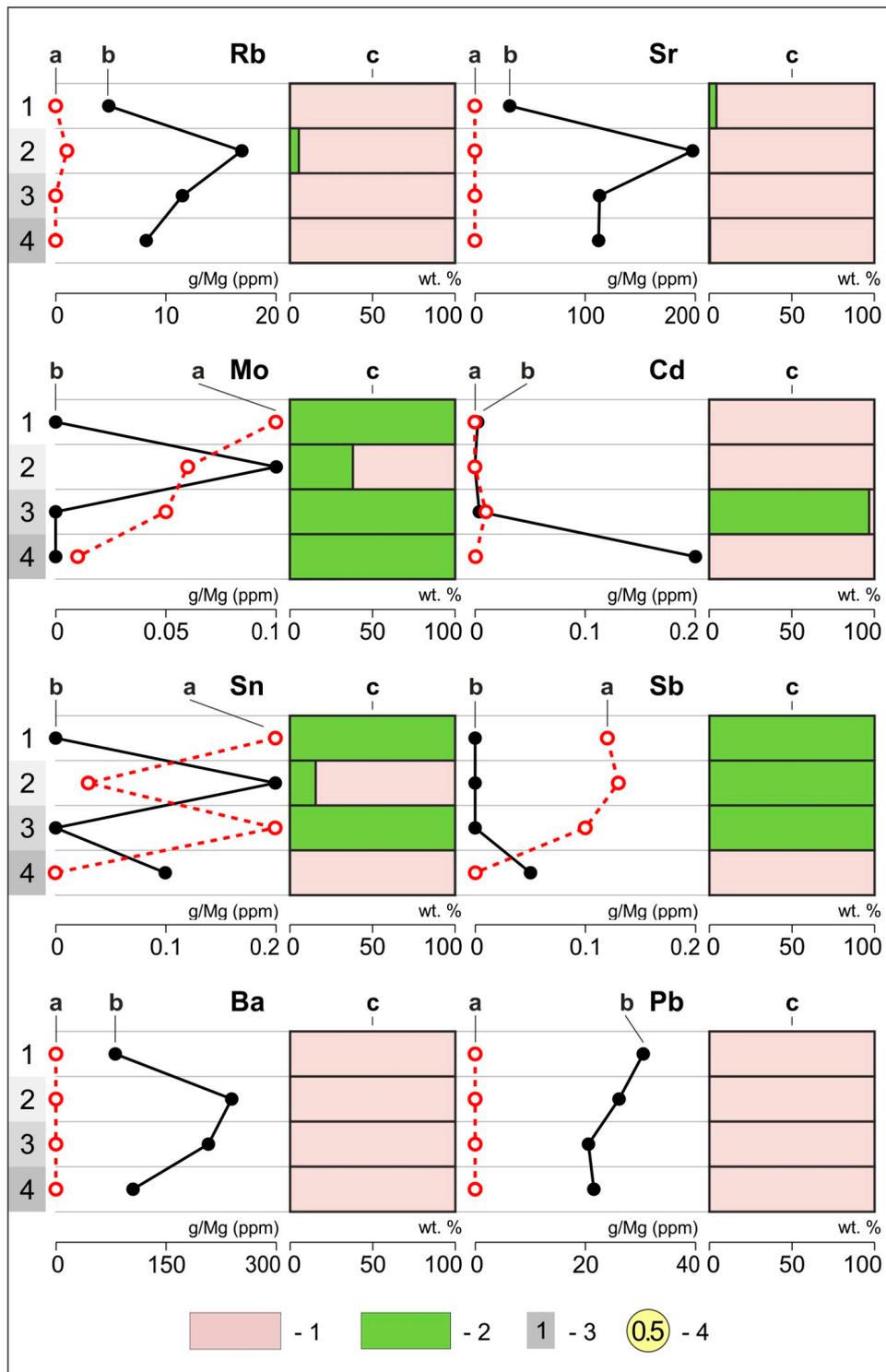


Figure 4. Cont.



**Figure 4.** The content of elements in the organic (a) and mineral matter (b) in the coal and the role of organic and mineral matter in concentrating the elements in the coal (c). 1—mineral matter; 2—organic matter; 3—lithostratigraphical sequence of the USCBB (1—Cracow Sandstone Series, 2—Mudstone Series, 3—Upper Silesian Sandstone Series, 4—Paralic Series); and 4—ratio of concentration Sr to Ba in the coal.

**Table 1.** Petrographical and physico-chemical characteristics of the researched coal from the USCB.

| Component                      | Researched Coal           | World Coal Deposit             |
|--------------------------------|---------------------------|--------------------------------|
|                                | <b>In coal</b>            |                                |
| Vitrinite (vol. %)             | 62.7 (66.8) *             | 68 [56]                        |
| Liptinite (vol. %)             | 7.7 (8.2) *               | 12 [56]                        |
| Inertinite (vol. %)            | 23.4 (25.0) *             | 20 [56]                        |
| Mineral matter (vol. %) **     | 6.2                       | 5.4 [57], 8.97 [58]            |
| Reflectance (%)                | 0.74                      | 0.58–0.74 [58], 0.66–0.92 [59] |
| Ash yield (wt.%)               | 11.60                     | 11.19 [58], 12.40 [60]         |
| Total sulphur (wt.%)           | 1.16                      | 1.71 [61] 1.24 [62], 1.00 [63] |
| Sulphate sulphur (wt.%)        | 0.21                      | 0.12 [62], 0.10 [64]           |
| Pyritic sulphur (wt.%)         | 0.52                      | 0.52 [62], 0.91 [64]           |
| Organic sulphur (wt.%)         | 0.43                      | 0.60 [62], 0.31 [64]           |
| V                              | 31.7                      | 28 ± 1 [38]                    |
| Cr                             | 8.7                       | 17 ± 1 [38]                    |
| Mn                             | 102.8                     | 71 ± 5 [38]                    |
| Co                             | 6.8                       | 6.0 ± 0.2 [38]                 |
| Ni                             | 13.9                      | 17 ± 1 [38]                    |
| Cu                             | 10.6                      | 16 ± 1 [38]                    |
| Zn                             | 56.8                      | 28 ± 2 [38]                    |
| As                             | 3.9                       | 9.0 ± 0.7 [38]                 |
| Rb                             | 13.8                      | 18 ± 1 [38]                    |
| Sr                             | 126.8                     | 100 ± 7 [38]                   |
| Mo                             | 0.1                       | 2.1 ± 0.1 [38]                 |
| Ag                             | <0.01                     | 0.100 ± 0.016 [38]             |
| Cd                             | 0.10                      | 0.20 ± 0.04 [38]               |
| Sn                             | 0.1                       | 1.4 ± 0.1 [38]                 |
| Sb                             | 0.1                       | 1.00 ± 0.09 [38]               |
| Ba                             | 171.6                     | 150 ± 10 [38]                  |
| Pb                             | 23.6                      | 9.0 ± 0.7 [38]                 |
|                                | <b>In coal ash (wt.%)</b> |                                |
| SiO <sub>2</sub>               | 32.12                     | 34.04 [57], 10–45 [61]         |
| TiO <sub>2</sub>               | 0.83                      | 0.88 ± 0.03 [38]               |
| Al <sub>2</sub> O <sub>3</sub> | 20.66                     | 22.90 [57], 1–11 [61]          |
| Fe <sub>2</sub> O <sub>3</sub> | 15.85                     | 23.45 [57], 1.5–5.5 [61]       |
| MgO                            | 4.48                      | 4.06 [57], 1–20 [61]           |
| CaO                            | 9.99                      | 9.17 [57], 2–45 [61]           |
| Na <sub>2</sub> O              | 1.29                      | 3.03 [57], 0.2–5 [61]          |
| K <sub>2</sub> O               | 1.43                      | 1.92 [57], 0.1–2.5 [61]        |
| P <sub>2</sub> O <sub>5</sub>  | 0.688                     | 0.344 ± 0.022 [38]             |
| SO <sub>3</sub>                | 12.66                     | 5–20 [61]                      |

\* Coal without mineral matter. \*\* Mineral matter composition (vol. %): clays = 1.7, carbonates = 1.8, quartz = 0.3, sulphides = 2.4, including the native minerals (chalcopyrite + galena + sphalerite < 0.1%).

In comparison with the average content of the oxides of the major elements in coal ash of other deposits around the world [38,57,61], the content of Fe<sub>2</sub>O<sub>3</sub> (15.85%), Al<sub>2</sub>O<sub>3</sub> (20.66%), and P<sub>2</sub>O<sub>5</sub> (0.688%; Table 1) in the tested USCB coal is high. The Mn, Zn, Sr, Ba, and Pb content in the USCB coal is greater, the Cr, Ni, Cu, As, Rb, Mo, Ag, Cd, and Sn content in coal is lower, and the content of V and C<sub>o</sub> in the coal is similar to the content of the aforementioned elements in hard coals from deposits around the world.

**Table 2.** The values of the correlation coefficients, expressing the dependence between the petrographic and chemical composition of the coal/coal ash and the content of the trace elements in the coal of the whole basin and from a part of the USCB.

| Element | USCB                                     |  |  |   |
|---------|--|--|--|---|
|         | General                                  | Western Part                             | Central Part                             | Eastern Part                            |
| V       | V-Cl * = 0.63                            | V-Cl = 0.66                              | V-Vt = 0.33                              | V-SiO <sub>2</sub> = 0.76               |
|         | V-SiO <sub>2</sub> = 0.77                | V-SiO <sub>2</sub> = 0.78                | V-Cl = 0.76                              | V-Al <sub>2</sub> O <sub>3</sub> = 0.69 |
|         | V-Al <sub>2</sub> O <sub>3</sub> = 0.65  | V-Al <sub>2</sub> O <sub>3</sub> = 0.82  | V-SiO <sub>2</sub> = 0.77                | V-TiO <sub>2</sub> = 0.81               |
|         | V-K <sub>2</sub> O = 0.71                | V-K <sub>2</sub> O = 0.74                | V-Al <sub>2</sub> O <sub>3</sub> = 0.61  | V-So = 0.71                             |
|         | V-TiO <sub>2</sub> = 0.72                | V-TiO <sub>2</sub> = 0.57                | V-K <sub>2</sub> O = 0.72                |   |
|         |  | V-So = 0.52                              | V-TiO <sub>2</sub> = 0.60                |   |
|         |  |  | V-So = 0.36                              |   |
| Cr      | Cr-Cl = 0.39                             | Cr-SiO <sub>2</sub> = 0.53               | Cr-Cl = 0.46                             |   |
|         | Cr-SiO <sub>2</sub> = 0.33               | Cr-Al <sub>2</sub> O <sub>3</sub> = 0.43 | Cr-SiO <sub>2</sub> = 0.45               |   |
|         | Cr-Al <sub>2</sub> O <sub>3</sub> = 0.43 | ( <i>p</i> = 0.055)                      | Cr-Al <sub>2</sub> O <sub>3</sub> = 0.48 |   |
|         | Cr-K <sub>2</sub> O = 0.35               | Cr-K <sub>2</sub> O = 0.48               | Cr-K <sub>2</sub> O = 0.43               |   |
|         | Cr-TiO <sub>2</sub> = 0.40               | Cr-TiO <sub>2</sub> = 0.44               | Cr-TiO <sub>2</sub> = 0.49               |   |
| Mn      | Mn-Cb = 0.46                             | Mn-CaO = 0.41                            | Mn-L = 0.33                              | Mn-Cb = 0.97                            |
|         | Mn-CaO = 0.56                            | ( <i>p</i> = 0.066)                      | Mn-Cb = 0.25                             | Mn-CaO = 0.80                           |
|         | Mn-MgO = 0.46                            | Mn-MgO = 0.46                            | Mn-CaO = 0.52                            | Mn-MgO = 0.93                           |
|         |  |  | Mn-MgO = 0.33                            |   |
|         |  |  | Mn-Ss = 0.35                             |   |
|         |  |  | Mn-Sp = 0.62                             |   |
| Co      | Co-Sf = 0.30                             | Co-SiO <sub>2</sub> = 0.37               | Co-Cb = 0.30                             |   |
|         |  | ( <i>p</i> = 0.101)                      |  |   |
|         |  | Co-TiO <sub>2</sub> = 0.58               |  |   |
|         |  | Co-Ss = 0.51                             |  |   |
| Ni      | Ni-L = 0.35                              | Ni-SiO <sub>2</sub> = 0.47               | Ni-L = 0.28                              |   |
|         | Ni-Sf = 0.35                             | Ni-TiO <sub>2</sub> = 0.56               | Ni-Sf = 0.27                             |   |
| Cu      | Cu-SiO <sub>2</sub> = 0.25               | Cu-SiO <sub>2</sub> = 0.55               | Cu-Cl = 0.27                             |   |
|         | Cu-Al <sub>2</sub> O <sub>3</sub> = 0.29 | Cu-Al <sub>2</sub> O <sub>3</sub> = 0.52 | Cu-Sf = 0.40                             |   |
|         | Cu-K <sub>2</sub> O = 0.31               | Cu-TiO <sub>2</sub> = 0.44               | Cu-TiO <sub>2</sub> = 0.29               |   |
| Zn      |  | Zn-Sf = 0.47                             |  |   |
| As      | As-Sf = 0.33                             | As-Sf = 0.68                             | As-Ss = 0.33                             |   |
|         | As-Sp = 0.45                             | As-Sp = 0.51                             | As-Sp = 0.35                             |   |
|         | As-Fe <sub>2</sub> O <sub>3</sub> = 0.33 |  | As-So = 0.30                             |   |
| Rb      | Rb-Cl = 0.73                             | Rb-Cl = 0.74                             | Rb-Cl = 0.81                             | Rb-K <sub>2</sub> O = 0.69              |
|         | Rb-Cb = 0.43                             | Rb-Cb = 0.45                             | Rb-SiO <sub>2</sub> = 0.76               | Rb-So = 0.67                            |
|         | Rb-SiO <sub>2</sub> = 0.74               | Rb-SiO <sub>2</sub> = 0.57               | Rb-Al <sub>2</sub> O <sub>3</sub> = 0.56 |   |
|         | Rb-Al <sub>2</sub> O <sub>3</sub> = 0.62 | Rb-Al <sub>2</sub> O <sub>3</sub> = 0.58 | Rb-K <sub>2</sub> O = 0.81               |   |
|         | Rb-K <sub>2</sub> O = 0.76               | Rb-K <sub>2</sub> O = 0.74               | Rb-TiO <sub>2</sub> = 0.50               |   |
|         | Rb-TiO <sub>2</sub> = 0.65               | Rb-TiO <sub>2</sub> = 0.44               |  |   |
| Sr      | Sr-Cl = 0.52                             | Sr-Vt = 0.49                             | Sr-Cl = 0.41                             | Sr-L = 0.68                             |
|         | Sr-Cb = 0.37                             | Sr-Cl = 0.42                             | Sr-SiO <sub>2</sub> = 0.52               | Sr-K <sub>2</sub> O = 0.75              |
|         | Sr-SiO <sub>2</sub> = 0.59               | ( <i>p</i> = 0.056)                      | Sr-Al <sub>2</sub> O <sub>3</sub> = 0.52 |   |
|         | Sr-Al <sub>2</sub> O <sub>3</sub> = 0.64 | Sr-Al <sub>2</sub> O <sub>3</sub> = 0.58 | Sr-K <sub>2</sub> O = 0.55               |   |
|         | Sr-K <sub>2</sub> O = 0.65               | Sr-K <sub>2</sub> O = 0.42               | Sr-TiO <sub>2</sub> = 0.49               |   |
|         | Sr-TiO <sub>2</sub> = 0.54               | Sr-P <sub>2</sub> O <sub>5</sub> = 0.63  | Sr-P <sub>2</sub> O <sub>5</sub> = 0.48  |   |
|         | Sr-P <sub>2</sub> O <sub>5</sub> = 0.64  |  |  |   |

Table 2. Cont.

| Element | USCB  |   |  |                             |
|---------|---|---|--|-----------------------------|
|         | General   | Western Part  | Central Part   | Eastern Part                |
| Mo      | Mo-Na <sub>2</sub> O = 0.62   | Mo-Na <sub>2</sub> O = 0.58   |  | Mo-Na <sub>2</sub> O = 0.99 |
| Cd      | Cd-Sf = 0.35<br>Cd-L = 0.45<br>Cd-CaO = 0.34<br>Cd-MgO = 0.34   |   | Cd-L = 0.37<br>Cd-Sf = 0.43  |                             |
| Sn      | Sn-I = 0.39<br>Sn-Na <sub>2</sub> O = 0.55  | Sn-L = 0.36<br>( <i>p</i> = 0.105)<br>Sn-Na <sub>2</sub> O = 0.67   | Sn-I = 0.38<br>Sn-Na <sub>2</sub> O = 0.35   | Sn-Na <sub>2</sub> O = 0.88 |
| Sb      |   | Sb-L = 0.34<br>( <i>p</i> = 0.128)<br>Sb-Na <sub>2</sub> O = 0.67   |  | Sb-Na <sub>2</sub> O = 0.96 |
| Ba      | Ba-Cl = 0.43<br>Ba-SiO <sub>2</sub> = 0.57<br>Ba-Al <sub>2</sub> O <sub>3</sub> = 0.54<br>Ba-K <sub>2</sub> O = 0.58<br>Ba-TiO <sub>2</sub> = 0.59<br>Ba-P <sub>2</sub> O <sub>5</sub> = 0.41 | Ba-Cl = 0.52<br>Ba-Al <sub>2</sub> O <sub>3</sub> = 0.47<br>Ba-K <sub>2</sub> O = 0.59  | Ba-Cl = 0.40<br>Ba-SiO <sub>2</sub> = 0.49<br>Ba-Al <sub>2</sub> O <sub>3</sub> = 0.41<br>Ba-K <sub>2</sub> O = 0.48<br>Ba-TiO <sub>2</sub> = 0.42 |                             |
| Pb      | Pb-Sf = 0.53<br>Pb-Sp = 0.43<br>Pb-Ss = 0.36  | Pb-Sf = 0.42<br>( <i>p</i> = 0.059)<br>Pb-SiO <sub>2</sub> = 0.53<br>Pb-Al <sub>2</sub> O <sub>3</sub> = 0.46<br>Pb-TiO <sub>2</sub> = 0.50 | Pb-Sf = 0.44   | Pb-Sp = 0.69                |

\* Cb—carbonates; Cl—clays; Q—quartz; I—inertinite; L—liptinite; Sf—sulphides; Sp—pyritic sulphur; Ss—sulphate sulphur; Vt—vitrinite; SiO<sub>2</sub> ... P<sub>2</sub>O<sub>5</sub>—major oxides.

**Table 3.** Values of the coefficient of correlation expressing the dependence between the petrographic and chemical composition of coal/coal ash and the content of the trace elements in the coal of the lithostratigraphic series of the USCB.

| Element | CSS*                                     | MS*                                      | USSS*  | PS*                                     |
|---------|--|--|--|---|
| V       | V-SiO <sub>2</sub> ** = 0.55             | V-Cl = 0.66                              | V-Vt = 0.59  | V-Vt = 0.42                             |
|         | V-K <sub>2</sub> O = 0.86                | V-Cb = 0.37                              | V-Cl = 0.58  | V-Cl = 0.72                             |
|         |  | V-SiO <sub>2</sub> = 0.82                | V-Cb = 0.38  | V-SiO <sub>2</sub> = 0.65               |
|         |  | V-Al <sub>2</sub> O <sub>3</sub> = 0.62  | V-SiO <sub>2</sub> = 0.82                                | V-Al <sub>2</sub> O <sub>3</sub> = 0.69 |
|         |  | V-K <sub>2</sub> O = 0.81                | V-Al <sub>2</sub> O <sub>3</sub> = 0.79                  | V-K <sub>2</sub> O = 0.62               |
|         |  | V-TiO <sub>2</sub> = 0.60                | V-K <sub>2</sub> O = 0.75<br>V-TiO <sub>2</sub> = 0.67   | V-TiO <sub>2</sub> = 0.74               |
| Cr      | Cr-Vt = 0.86                             |  | Cr-Cl = 0.59   | Cr-Na <sub>2</sub> O = 0.42             |
|         | Cr-K <sub>2</sub> O = 0.77               |  | Cr-SiO <sub>2</sub> = 0.57                               | Cr-TiO <sub>2</sub> = 0.40              |
|         | Cr-Fe <sub>2</sub> O <sub>3</sub> = 0.83 |  | Cr-Al <sub>2</sub> O <sub>3</sub> = 0.55                 |   |
|         |  |  | Cr-K <sub>2</sub> O = 0.54<br>Cr-TiO <sub>2</sub> = 0.60 |   |
| Mn      | Mn-Cb = 0.92                             | Mn-Fe <sub>2</sub> O <sub>3</sub> = 0.42 | Mn-L = 0.34  | Mn-Cb = 0.46                            |
|         | Mn-CaO = 0.86                            | Mn-CaO = 0.36                            | Mn-CaO = 0.62  | Mn-CaO = 0.54                           |
|         | Mn-MgO = 0.94                            | Mn-MgO = 0.43                            | Mn-MgO = 0.59  | Mn-MgO = 0.42                           |
|         |  | Mn-Cb = 0.33<br>( <i>p</i> = 0.079)      |  | Mn-Sp = 0.64                            |
|         |  |  |  |   |

Table 3. Cont.

| Element | CSS*   | MS*   | USSS*  | PS*   |
|---------|--|---|--|---|
| Co      | Co-Fe <sub>2</sub> O <sub>3</sub> = 0.73<br>Co-K <sub>2</sub> O = 0.85   | Co-Vt = 0.31<br>( <i>p</i> = 0.100)   | Co-Sf = 0.38<br>Co-Vt = 0.46<br>Co-SiO <sub>2</sub> = 0.69<br>Co-Al <sub>2</sub> O <sub>3</sub> = 0.45<br>Co-TiO <sub>2</sub> = 0.62   | Co-Cb = 0.41  |
| Ni      | Ni-Vt = 0.84<br>Ni-Fe <sub>2</sub> O <sub>3</sub> = 0.87   |   | Ni-Cl = 0.38<br>Ni-Cb = 0.66<br>Ni-Sf = 0.59<br>Ni-SiO <sub>2</sub> = 0.76<br>Ni-TiO <sub>2</sub> = 0.68   | Ni-Sf = 0.56<br>Ni-L = 0.72   |
| Cu      | Cu-TiO <sub>2</sub> = 0.63   | Cu-Al <sub>2</sub> O <sub>3</sub> = 0.40<br>Cu-P <sub>2</sub> O <sub>5</sub> = 0.46   | Cu-Vt = 0.48<br>Cu-SiO <sub>2</sub> = 0.49<br>Cu-Al <sub>2</sub> O <sub>3</sub> = 0.60<br>Cu-K <sub>2</sub> O = 0.49<br>Cu-TiO <sub>2</sub> = 0.57                                 | Cu-Cl = 0.49<br>Cu-SiO <sub>2</sub> = 0.45  |
| Zn      | Zn-CaO = 0.52<br>( <i>p</i> = 0.072)<br>Zn-Na <sub>2</sub> O = 0.75  | Zn-Sf = 0.59<br>Zn-Fe <sub>2</sub> O <sub>3</sub> = 0.59  |  |   |
| As      |  | As-A = 0.36<br>As-So = 0.41   | As-Cb = 0.45<br>As-Sp = 0.37<br>As-Ss = 0.52   | As-Sf = 0.40<br>As-Sp = 0.48<br>As-Cd = 0.70<br>As-Ss = 0.65  |
| Rb      | Rb-SiO <sub>2</sub> = 0.65<br>Rb-Al <sub>2</sub> O <sub>3</sub> = 0.49<br>( <i>p</i> = 0.087)<br>Rb-K <sub>2</sub> O = 0.79      | Rb-Cl = 0.68<br>Rb-SiO <sub>2</sub> = 0.78<br>Rb-Al <sub>2</sub> O <sub>3</sub> = 0.55<br>Rb-K <sub>2</sub> O = 0.87<br>Rb-TiO <sub>2</sub> = 0.48  | Rb-Vt = 0.45<br>Rb-Cl = 0.71<br>Rb-Cb = 0.41<br>Rb-SiO <sub>2</sub> = 0.68<br>Rb-Al <sub>2</sub> O <sub>3</sub> = 0.66<br>Rb-K <sub>2</sub> O = 0.84<br>Rb-TiO <sub>2</sub> = 0.51 | Rb-Cl = 0.61<br>Rb-SiO <sub>2</sub> = 0.71<br>Rb-Al <sub>2</sub> O <sub>3</sub> = 0.57<br>Rb-K <sub>2</sub> O = 0.69<br>Rb-TiO <sub>2</sub> = 0.68  |
| Sr      | Sr-I = 0.80<br>Sr-SiO <sub>2</sub> = 0.79<br>Sr-Al <sub>2</sub> O <sub>3</sub> = 0.77<br>Sr-P <sub>2</sub> O <sub>5</sub> = 0.85 | Sr-Cb = 0.62<br>Sr-SiO <sub>2</sub> = 0.62<br>Sr-Al <sub>2</sub> O <sub>3</sub> = 0.38<br>Sr-K <sub>2</sub> O = 0.68<br>Sr-TiO <sub>2</sub> = 0.71<br>Sr-P <sub>2</sub> O <sub>5</sub> = 0.73 | Sr-Vt = 0.47<br>Sr-Cl = 0.37<br>Sr-SiO <sub>2</sub> = 0.42<br>Sr-Al <sub>2</sub> O <sub>3</sub> = 0.55<br>Sr-K <sub>2</sub> O = 0.53<br>Sr-P <sub>2</sub> O <sub>5</sub> = 0.50    | Sr-Vt = 0.40<br>Sr-Cl = 0.75<br>Sr-SiO <sub>2</sub> = 0.66<br>Sr-Al <sub>2</sub> O <sub>3</sub> = 0.84<br>Sr-K <sub>2</sub> O = 0.56<br>Sr-TiO <sub>2</sub> = 0.64<br>Sr-P <sub>2</sub> O <sub>5</sub> = 0.64 |
| Mo      | Mo-Na <sub>2</sub> O = 0.89  | Mo-P <sub>2</sub> O <sub>5</sub> = 0.57<br>Mo-Na <sub>2</sub> O = 0.65  | Mo-I = 0.55<br>( <i>p</i> = 0.062)<br>Mo-CaO = 0.61<br>Mo-MgO = 0.70   | Mo-Na <sub>2</sub> O = 0.87   |
| Cd      |  | Cd-I = 0.281<br>( <i>p</i> = 0.103)<br>Cd-Cl = 0.65<br>Cd-Fe <sub>2</sub> O <sub>3</sub> = 0.46<br>Cd-P <sub>2</sub> O <sub>5</sub> = 0.38  | Cd-Cl = 0.81<br>Cd-Q = 0.85  | Cd-Sf = 0.49<br>Cd-L = 0.48   |
| Sn      | Sn-Na <sub>2</sub> O = 0.81<br>Sn-MgO = 0.70   | Sn-P <sub>2</sub> O <sub>5</sub> = 0.47   | Sn-I = 0.62<br>Sn-MgO = 0.58<br>Sn-Na <sub>2</sub> O = 0.35  | Sn-Na <sub>2</sub> O = 0.87   |

Table 3. Cont.

| Element | CSS*                                     | MS*                                      | USSS*                                    | PS*                                      |
|---------|--|--|--|--|
| Sb      | Sb-Vt = 0.80                             | Sb-Cl = 0.58                             |  | Sb-Na <sub>2</sub> O = 0.78              |
|         | Sb-Sf = 0.84                             | Sb-Fe <sub>2</sub> O <sub>3</sub> = 0.43 |  |  |
|         | Sb-K <sub>2</sub> O = 0.81               | Sb-P <sub>2</sub> O <sub>5</sub> = 0.44  |  |  |
| Ba      | Ba-Vt = 0.82                             | Ba-K <sub>2</sub> O = 0.40               | Ba-Vt = 0.37                             | Ba-SiO <sub>2</sub> = 0.41               |
|         | Ba-Fe <sub>2</sub> O <sub>3</sub> = 0.87 | Ba-TiO <sub>2</sub> = 0.47               | Ba-Cl = 0.57                             | Ba-Al <sub>2</sub> O <sub>3</sub> = 0.62 |
|         | Ba-K <sub>2</sub> O = 0.76               | Ba-P <sub>2</sub> O <sub>5</sub> = 0.41  | Ba-Cb = 0.40                             | Ba-K <sub>2</sub> O = 0.40               |
|         |  |  | Ba-SiO <sub>2</sub> = 0.48               | Ba-TiO <sub>2</sub> = 0.53               |
| Pb      |  |  | Ba-K <sub>2</sub> O = 0.51               | Ba-P <sub>2</sub> O <sub>5</sub> = 0.73  |
|         | Pb-Sp = 0.69                             | Pb-Sf = 0.61                             | Pb-Cb = 0.41                             | Pb-Sf = 0.72                             |
|         | Pb-Sf = 0.53                             | Pb-Sp = 0.70                             | Pb-SiO <sub>2</sub> = 0.65               | Pb-L = 0.60                              |
|         | ( <i>p</i> = 0.064)                      | Pb-St = 0.81                             | Pb-Al <sub>2</sub> O <sub>3</sub> = 0.45 |  |
|         | Pb-TiO <sub>2</sub> = 0.71               | Pb-Fe <sub>2</sub> O <sub>3</sub> = 0.49 | Pb-K <sub>2</sub> O = 0.37               |  |
|         | Pb-P <sub>2</sub> O <sub>5</sub> = 0.73  | ( <i>p</i> = 0.088)                      | Pb-TiO <sub>2</sub> = 0.65               |  |

CSS\*—Cracov Sandstone Series; MS—Mudstone Series; USSS—Upper Silesian Sandstone Series; PS—Paralic Series.  
 \*\* A—ash yield; Cb—carbonates; Cl—clays; I—inertinite; L—liptinite; Q—quartz; Sf—sulfides; S—organic sulphur;  
 Sp—pyritic sulphur; Ss—sulphate sulphur; Vt—vitrinite; SiO<sub>2</sub> ... P<sub>2</sub>O<sub>5</sub>—major oxides.

## 4.2. Mode of Occurrence of Trace Elements in Coal

### 4.2.1. General Trends

Based on the data presented in Figure 3, there was an observed affinity of V, Cr, Co, Ni, Cu, As, Rb, Sr, Cd, Ba, and Pb to mineral matter in the coal; an affinity of Zn, Mo, Sn, and Sb to organic matter; and an affinity of Mn both to organic matter and to mineral matter in the USCB coal. The analysis of the value of the correlation coefficient between the content of the petrographic components of the coal together with the content of oxides of the major elements in the tested coal throughout the USCB, and the content of the trace elements in the coal, provided further data (Table 2). There was an observed affinity of Co, Ni, As, Cd, and Pb to sulphides; an affinity of V, Cr, Cu, Rb, Sr, and Ba to clay minerals; an affinity of Mn, Rb, Sr, and Cd to carbonate minerals; an affinity of Sr and Ba to phosphates; an affinity of Ni and Cd to liptinite; and an affinity of Sn to inertinite in the USCB coal. A low value of the correlation coefficient, or a lack of any correlation, rendered it impossible to indicate affinity of Zn, Mo, and Sb to the petrographic components of the coal.

The aforementioned observations are similar to the results of tests of coal from different deposits of bituminous coal around the world [7–16,62–64]. The only observed variances concerned Ni, Cd, and Sn, i.e., in the tested coal, the elements are probably associated with liptinite and inertinite, and in coals of other deposits around the world, they are associated with sulphide minerals and clay minerals. It is worth mentioning that the content of Zn, Mo, and Sn in coal from deposits around the world is determined mainly by the amount and composition of sulphide minerals.

### 4.2.2. Lateral Variability

The data in Figure 3 indicate a strong and nearly constant or constant affinity of V, Cr, Co, As, Rb, Sr, Ba, and Pb to mineral matter in the coal, and a constant affinity of Sn to organic matter in the horizontal profile of the USCB coal. The correlation dependences, observed in Table 2, between the petrographic and chemical composition of coal, and the content of the trace elements in coal, confirm the nearly constant affinity of V, Cr, As, Rb, Ba, and Pb to mineral matter in the coal. There was an observed affinity of As and Pb to sulfides in coal in the western and central part of the USCB, as well as an affinity of Pb to the sulfides in the coal in the eastern part, and to clay minerals in the coal in the western part of the USCB. There is affinity of V, Cr, Rb, and Ba to the clay minerals in the coal of the western and central part of the USCB, and of V in the eastern part of the USCB. The data in Table 2 suggest that the affinity of Co and Sr to mineral matter in coal is variable. There are differences in the

affinity of Sn to organic matter in the USCB coal, as an affinity of Co to clay minerals in coal in the western part of the USCB and an affinity to carbonate minerals in the coal in the central part of the basin were observed. There was an observed affinity of Sr to clay minerals and vitrinite in coal in the western part of the basin; an affinity of Sr to clay minerals in coal in the central part of the basin; as well as an affinity of Sr to liptinite and K-rich substances in coal in the eastern part of the basin. Moreover, there was an affinity of Sn to liptinite in the coal of the western part of the USCB; to inertinite in the coal in the central part of the basin; and to Na-rich substances in the coal throughout the USCB.

There were observed significant lateral differences in the affinity of Mn, Ni, Cu, Zn, Mo, Cd, and Sb to mineral matter and organic matter in the USCB coal (Table 2 and Figure 3). There was an observed affinity of Ni and Cu to clay minerals in coal in the western part of the USCB; to clay minerals (only Cu) and to liptinite (Ni) in the coal in the central part of the basin; and an affinity of Cu and Ni to mineral matter and organic matter in the coal in the eastern part of the basin. Affinity of Mn to carbonates and organic matter in the coal of the whole basin and to sulfides in the coal of the central part of the basin was observed. There was an affinity of Mo to mineral matter in the coal in the eastern part of the basin; to Na-rich organic substance in the coal in the western part of the basin; and in general to organic matter in the coal in the central part of the USCB. There was an observed affinity of Sb to liptinite in the coal in the western part of the basin; an affinity of Sb in similar proportions to the organic matter and mineral matter in the coal in the central part of the basin; and Na-rich organic matter in the coal in the eastern part of the basin. There was an observed affinity of Zn to sulfides in the western part of the USCB; to organic matter in coal in the central part of the basin; as well as to mineral matter in the coal in the eastern part of the basin. There is probably also affinity of Cd to sulfides and liptinite in the coal in the central part of the USCB.

#### 4.2.3. Vertical Variability

There were observed changes in the affinity of Cr, Mn, Co, Ni, Cu, Zn, Mo, Cd, Sn, and Pb to mineral matter and organic matter in the coal in the lithostratigraphic profile of the USCB, i.e., the Cracow Sandstone Series (CSS), through the Mudstone Series (MS), and the Upper Silesian Sandstone Series (USSS) to the Paralic Series (PS) (Figure 4 and Table 3). There was an observed affinity of Co and Cd to mineral matter containing mainly Fe and K compounds (Co) in the coal of the CSS; affinity of Cd and Co to organic matter containing mainly inertinite (Cd) and vitrinite (Co), as well as clay minerals and Fe and P compounds (Cd) in the coal of the MS; affinity of Cd and Co to organic matter and clay minerals (Cd) and sulfides, clay minerals and vitrinite (Co) in the coal of the USSS; and an affinity of Cd and Co to sulphide-rich mineral matter (Cd), carbonates (Co), and, probably, liptinite (Cd) in the coal of the PS. There was an observed affinity of Cr to vitrinite-rich organic matter as well as Fe and K compounds in the coal of the CSS; the general affinity of Cr to organic matter in the coal of the MS; affinity of Cr to clay mineral-rich mineral matter and subordinately to organic matter in the coal of the USSS; as well as affinity of Cr to mineral matter containing Na and Ti compounds in the coal of the PS. There is affinity of Ni and Cu to Ti compounds (Cu), as well as to vitrinite and Fe compounds (Ni) in the coal of the CSS; general affinity of Ni and Cu to organic matter in the coal of the MS; affinity of Ni and Cu to mainly clay mineral-rich mineral matter (Ni and Cu) and carbonates (Ni) and subordinately to organic matter containing vitrinite (Cu) in the coal of the USSS; as well as affinity of Ni and Cu to clay mineral-rich mineral matter (Cu) and sulfides (Ni) and to liptinite in the coal of the PS. There was an observed affinity of Mn to carbonates and organic matter in the coal of the CSS and the MS; affinity of Mn to liptinite and, subordinately, to carbonates in the coal of the USSS; as well as affinity of Mn to carbonates, sulfides and, subordinately, to organic matter in the coal of the PS. There was an observed affinity of Mo to organic matter in the coal of the CSS; affinity of Mo to Na and P compounds in the coal of the MS; affinity of Mo to inertinite-rich organic matter together with Mg and Ca compounds in the coal of the USSS; as well as affinity of Mo to organic matter in the coal of the PS. There is affinity of Sn and Sb to vitrinite-rich organic matter, K (only Sb), Na, and Mg compounds (Sn), and probably also to sulfides (Sb) in the coal of the CSS; affinity of Sn and Sb to Fe- and P-rich

organic matter, clay minerals (Sb), and P compounds in the coal of the MS; affinity of Sn and Sb to organic matter containing mainly inertinite and Mg and Na compounds (Sn) in the coal of the USSS; as well as affinity of Sn and Sb to mineral matter in the coal of the PS. There was an observed affinity of Zn to mineral matter in the coal of the CSS and the PS; affinity of Zn to organic matter and sulfides in the coal of the MS; as well as affinity of Zn to organic matter in the coal of the USSS.

There was also no observed variability and, simultaneously, a constant strong affinity of V, As, Rb, Sr, Ba, and Pb to mineral matter in the coal in the lithostratigraphic profile of the USCB (Figure 4), whereas the affinity of the elements to the given petrographic component groups in the coal of the USCB was differentiated. (Figure 4 and Table 3). There was an observed affinity of the aforementioned elements to clay minerals (Rb and Sr), sulfides (Pb), phosphates (Sr and Pb), and mineral matter enriched with Fe<sub>2</sub>O<sub>3</sub>, and/or to the K-rich mineral matter (V, Rb, and Ba) with impurities of vitrinite (Ba) and inertinite (Sr) in the coal of the CSS. There was an observed affinity of V, As, Rb, Sr, Ba, and Pb to clay mineral-rich mineral matter (V, Rb, Sr, and Ba), phosphate minerals (only Sr and Ba), carbonate minerals (V and Sr), and sulphide minerals (Pb) in the coal of the MS. There was observed affinity of V, As, Rb, Ba, and Pb to carbonates; affinity of V, Rb, Sr, Ba, and Pb to clay minerals; affinity of Sr to phosphates; affinity of As to sulfides and/or sulphates; and affinity of V, Rb, Sr, and Ba to vitrinite in the coal of the USSS. There was also observed affinity of As and Pb to sulphide-rich mineral matter; affinity of V, Rb, Sr, and Ba to clay minerals; affinity of Sr and Ba to phosphate minerals; affinity of As to carbonates; affinity of V and Sr to vitrinite; and affinity of Pb to mineral matter and liptinite in the coal of the PS.

#### 4.2.4. Interpretation of Variability in the Mode of Occurrence of Elements in the Coal

The observed strong affinity of the trace elements to mineral matter in the coal of the USCB is probably a result of epigenetic and diagenetic mineralisation in the coal seams. The increased content of Mn, Zn, As, and Pb in coal of the USCB and the dominant role of the mineral matter (mainly carbonates and sulfides, Table 2) in concentrating Mn, Zn, As, and Pb in coal of the eastern rather than in the western and central part of the basin (Figure 3) indicates the significant role of epigenetic processes. These processes led to the formation of Triassic Carbonate–Hosted Zinc–Lead Deposits in Upper Silesia [47,65]. Some of the current content of Rb, Sr, and Ba in the tested coal, especially in the Mudstone Series, probably comes from the epigenetic mineralization of sulphates, which was observed in coal seams and their vicinity in the USCB a long time ago. No sulphate minerals in the coal were observed in this work. However, their presence in coal is very likely, due to the identification of sulphate minerals more than once [66,67]. The manifestations of epigenetic carbonate and sulphide mineralization enriching carbon in the USCB in Mn, Zn, As and Pb observed in this work confirm earlier reports Dai et al. [68]. The quoted authors found high levels of Mn, Cu, Ni, Zn, and Pb in the veins cutting through coal.

A large share of the content of V, Co, and Cu in coal in the western part of the basin and some of the content of Mn, Ni, Co, Cu, As, Cd, and Sb in coal of the Paralic Series (with higher rank coal), is probably of diagenetic origin. The elements concentrated in the mineral matter probably as a result of the carbonisation of the organic matter, when carbon atoms condense in a coal macromolecule and the destruction of the metal–organic compounds intensifies [69]. The concentration of the elements is higher in the low coalification organic matter of peats and lignites than in bituminous coal [3,70–72]. Low durability of complex bindings of the discussed elements and the humid environment, with simultaneous excess of sulphur ions, probably contributed, at the initial stage of diagenesis, to crystallising the sulfides (chalcopyrite, sphalerite, and galena) identified in the tested coals. At the final stage of diagenesis, iron ions, which are harder to release from metal–organic compounds (from chalcophile elements), probably formed the substance from which the crystallised sulfides and carbonates were observed among the macerals of the coals of the western part of the USCB, as well as in the Paralic Series of the USCB [15,73]. The low coalification of the organic matter of coals contains (apart from chalcophile elements) also elements commonly considered to be lithophile ones, e.g., V, Ti,

Cr, and Zr [71]. As a result of the decarboxylation of organic matter, the elements bind into various aluminosilicate compounds in the humid environment. Then, focal concentrations of clay minerals and microcrystalline grains of oxides and oxide-hydroxides are formed from the compounds [72,74].

In the vertical profile of the USCB there are differences in the conditions of sedimentation of Carboniferous rocks and coal seams, i.e., from gravel and sand rocks of the CSS, through clay and mudrocks of the MS and clay and sandstone rocks of the USSS; i.e., a complex of rocks and coal seams formed during the conditions of lacustrine-terrestrial sedimentation, into the complex of Carboniferous clay rocks of the PS that formed in the conditions of shallow marine sedimentation [43,45]. The lithological changes in the coal seams are accompanied by changes in the content of the oxides of the main ash-forming elements [75] and changes in the content of the trace elements [76]. Differences in the conditions of formation of coal seams were expressed in the article with the ratio of the content of Sr/Ba < 1 for coal of the CSS, the MS, and the USSS, as well as the ratio of content Sr/Ba > 1 for coals of the PS (Figure 4). Following the interpretation of the values of Sr/Ba assumed according to [3], the tested coal samples representing the CSS, the MS, and the USSS were formed in the conditions of limnic sedimentation, and the PS coal samples were formed in the conditions of paralic sedimentation.

The observed lateral and vertical changes in affinity of certain trace elements to mineral matter and organic matter in coal within one basin, supplement the hitherto observations concerning changes in the mode of occurrence of elements within the profile of a single coal seam [77,78], differences between the mode of occurrence of the elements in bituminous coal, and the mode in the sub-bituminous coal [5,10]. It seems that the changes in the mode of occurrence of elements in coal within a deposit and between coal deposits are a regularity.

The stronger affinity of the elements (V, Cr, Ni, Co, Cu, As, Rb, Sr, Cd, Ba, and Pb) to mineral matter than to organic matter (Zn, Mo, Sn, and Sb) in the tested coal (Figure 3) is thought to be a generally advantageous quality of coal if it is necessary to obtain a pure energy fuel, free of ecotoxic elements. Especially taking into consideration the fact that removing the elements from the macerals and from non-crystalline mineraloids, and elements with non-mineral associations from coal with gravity separation and flotation, is considered to be ineffective [1,79–83]. In comparison with flotation, it is better to remove most of the elements applying multi-stage flotation. The rate of removal of the thiophile and siderophile elements (Co, Ni, Cu, Zn, As, Cd, and Pb) from coal is greater than of lithophile elements (Sc, Rb, Ba, and Tl) [84]. Multistage preparation is the most effective method of separating toxic elements from coal. In turn, chalcophile elements, occurring in >50 µm epigenetic grains of sulfides, can be removed from coal with satisfying effectiveness (approximately 80%), applying gravity separation and/or flotation [24,81,85,86]. The removal rate of thalassophile elements (Ca, Mg, Na, Fe, Mn, Zn, B, and Sr) is high, while that of continental elements (Al, Pb, Ba, and Th) is low [87]. Still, the best solution for the environment is avoiding combustion of ecotoxic elements-rich coal, preceded by monitoring their content in raw coal. It was supposedly successfully conducted in the USA [88].

Summing up and assuming observed affinity of the elements to mineral matter and organic matter, as well as affinity to petrographic component groups of coal as the probable mode of occurrence of the elements in the coal of the USCB, it may be expected that it will be hard to (1) remove from coal only Mo, Sn, and Sb (which are associated with organic matter in the coal in the western part of the USCB); (2) remove Zn, Mo, and Sn from the coal of the central part of the basin; and (3) remove Sn and Sb from coal in the eastern part of the USCB. Moreover, it is going to be hard to remove Cr, Cu, Cd, Mo, Sn, and Sb from coal of the Cracow Sandstone Series; Cr, Mn, Ni, Co, Cu, Zn, Cd, and Sb from coal of the Mudstone Series; V, Mn, Zn, Mo, Cd, Sn, and Sb from coal of the Upper Silesian Sandstone Series; as well as Mo from coal of the Paralic Series (Figures 3 and 4, as well as Tables 2 and 3).

There are reservations concerning coal combustion in which the discussed elements are related, even slightly, to organic matter. There is a threat that the elements, together with flue gases, will be either released into the atmosphere or condensed on the particles of the fly ash. During coal combustion, the elements related to sulfides and organic matter show volatile properties. The volatility

of As, Se, and Cd may be caused by a reaction of the elements with the compounds of Cl, F, Na, or S. Even if the elements are not volatile, they are present in ash, mainly in form of oxides and sulphates, which may be easily removed from the waste through leaching. Mobility of Mo, U, V, and W may vary between 90% and 5%, depending on whether the elements are present in coal with an affinity to organic matter or heavy metals (U), sulfides (Mo) or clays (V). After the combustion, if the elements represent an affinity to organic matter, they are present in ash as oxides, which are mobile at neutral pH values (such as leaching). It is assumed that the elements in coal, related mainly to the organic and sulphide fraction, evaporate first, and then get easily adsorbed on fine particles as the flue gases cool down. Unlike the elements related to other minerals, they probably remain within the ash matrix or slowly evaporate [23,89–95].

The volatility of the elements varies, i.e., it is different at the beginning and during the main stage of combusting in Power Plants. For each element of different modes of occurrence, the variability depends on the coal rank and working conditions, especially the temperature of combustion [40,96,97]. Coefficients of enriching elements of high volatility (e.g., As, Hg, and Zn) in fly ash and bottom ash are low, which indicates the elements were released into the atmosphere together with flue gases [17,23,98–100]. Taking into account the aforementioned possible mode of occurrence of the analysed elements in the USCB coal (Figures 3 and 4, as well as Tables 2 and 3), it can be predicted that the aforementioned elements related to organic matter of the tested coal, as well as the elements related to sulfides will (Figures 3 and 4, as well as Tables 2 and 3), during coal combustion, be transported to the gas desulphurisation system and/or they will get intensively condensed on the fine particles of the fly ash and/or they will be released into the environment. The average temperature of coal combustion in Power Plants in Poland (960 °C, [101]; 1340 °C, [53]) is generally higher than the melting temperature of Zn, As, Rb, Sr, Ag, Cd, Sn, Sb, Ba, and Pb and lower than the melting temperature of V, Mn, Ni, Cr, Co, Cu, and Mo. It may be the cause that explains the high content of the first group of elements in fly ash and the high content of the other group of elements in slag.

Leachate, formed when the rainwater or surface water flows through mine waste dumps or interacts with the elements contained in a few-millimetre-thick layer of technogenic magnetic particles near the surface of the soil, as well as Al–Si microspheres in the emitted particles and landfilled fly ash, bottom ash, and slag, may turn out to be dangerous for the environment. Although the issue is not addressed in the article, it is worth remembering that forecasts of the yield of the extracted trace elements is influenced, among others, by their mode of occurrence in coal [2,10,18,29,102].

## 5. Conclusions

(1) The content of Mn, Zn, Sr, Ba, and Pb in the tested coal is greater; the content of Cr, Ni, Cu, As, Rb, Mo, Ag, Cd, and Sn in coal is lower; and the content of V and Co in coal is similar to the content of the elements in hard coal of deposits around the world.

(2) Sulfides probably determine the content of Ni, Co, As, Cd, and Pb in coal; clay minerals probably determine the content of V, Cr, Cu, Rb, Sr, and Ba in coal; carbonates probably determine the content of Mn, Rb, Sr, and Cd; phosphates probably determine the content of Sr and Ba; liptinite probably determines the content of Ni and Cd; inertinite probably determines the content of Sn; and organic matter probably has a decisive influence on the content of Zn, Mo, and Sb in coal.

(3) There was observed a significant and nearly constant or constant role of mineral matter in concentrating V, Cr, Co, As, Rb, Sr, Ba, and Pb in coal; a constant role of organic matter in concentrating Sn; and significant differences in the role of organic matter and mineral matter in concentrating Mn, Ni, Cu, Zn, Mo, Cd, and Sb in coal throughout the USCB.

(4) There were observed differences in the modes of occurrence of Cr, Mn, Ni, Co, Cu, Zn, Mo, Cd, Sn, and Sb in coal in the vertical profile of the USCB, as well as the invariable and constant significant role of mineral matter in concentrating V, As, Rb, Sr, Ba, and Pb in coal. Simultaneously, the role of the petrographic groups of the coal components in concentrating the elements in raw coal varied.

(5) It is believed that coal purification (coal enrichment) does not remove Mo, Sn, and Sb related to organic matter in coal of the western part of the USCB; Zn, Mo, and Sn from coal of the central part; Sn and Sb from coal of the eastern part of the USCB; Cr, Cu, Mo, Cd, Sn, and Sb from coal of the Cracow Sandstone Series; Cr, Mn, Ni, Co, Cu, Zn, Cd, and Sb from coal of the Mudstone Series; V, Mn, Zn, Mo, Cd, Sn, and Sb from coal of the Upper Silesian Sandstone Series; and Mo from coal of the Paralic Series.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2075-163X/10/5/422/s1>, Table S1: Results of performed analyses of the coal samples; Table S2: Results of analysis in coal samples after conversion into coal seams, data for Table 1; Table S3: Idea of CD function, example of calculations; Table S4: Calculation data and calculation results of the CD function for Part C, E and W of the USCB, data for Figure 3; Table S5: Calculation data and calculation results of the CD function for lithostratigraphic members of the USCB, data for Figure 4; Table S6: Pearson correlation coefficient calculated for coal samples/seams from the whole and parts of the USCB, data for Table 2; Table S7: Pearson correlation coefficient calculated for coal samples/seams from lithostratigraphic members of the USCB, data for Table 3.

**Funding:** This research received no external funding.

**Acknowledgments:** The author would like to thank L. Róg from the Central Mining Institute in Katowice (Poland) for performing petrographic coal analysis. The author thanks two anonymous reviewers that provided many helpful comments and suggestions.

**Conflicts of Interest:** The authors declare no conflict of interest.

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