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Toxic elements in carboniferous sedimentary rocks from the Upper Silesian Coal Basin

Introduction

Industry and human activity generate large amounts of waste material, particularly from mining and energy sectors. Some of this waste is placed in mine-tailing impoundments, while the remainder is used in road and engineering construction or for land reclamation (Różański 2019; Strzałkowska 2021). Trace elements contained in these wastes are often toxic. Knowledge of the geochemical composition of waste materials is of great importance due to the potential for the release of these elements into the environment. During storage and use, these waste materials can release contaminants through hypergenic processes (Yudovich and Ketris 2015; Migaszewski and Gałuszka 2016).

Impacts of mining waste may also occur due to geotechnical instability of mine--waste impoundments, water and wind erosion, the formation of acid leachate, and in-

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creased salinity. In the case of Carboniferous waste, there is also the risk of self-ignition within the deposit, releasing particulates that may contain toxic elements into the atmosphere.

Harmful elements may leach from the waste and migrate into the soil and water, contributing to environmental degradation. These toxic elements may include, inter alia, Pb, Cd, Co, Be, As, Sb, Se and Ta. The permissible maximum concentrations of these elements in water and soil have been specified in Ordinances of the Ministry of Environment dated 25 June 2021 (Ordinance ME 2011) and 1 September 2016 (Ordinance ME 2016).

As part of an integrated environmental protection system, determining the geochemical composition of rock material stored on mining waste impounds from a raw materials perspective is needed to accurately assess its suitability for use and potential impacts on the environment. Analysis of rare and trace elements in raw materials has become more frequent due to the potential presence of many elements that are harmful to the environment (Yudovich and Ketris 2015; Migaszewski and Gałuszka 2016).

In recent years, intensive drilling for the exploration of coking-coal resources has been carried out in the Upper Silesian Coal Basin (USCB). The material from the new boreholes can provide important data on the geochemistry of the Carboniferous series, including concentrations of toxic elements. Therefore, the main goals of this study were to:

◆ evaluate the geochemical characteristics of the Carboniferous coal-bearing series of the USCB;
◆ analyze the concentrations of selected toxic elements in the coal-bearing series of the USCB;
◆ examine correlations among the elements.

1. Toxic elements in sedimentary rocks

Harmful elements include potentially toxic elements (PTEs) in any concentration, such as As, Hg, Cd, Pb, and Be; higher concentrations of Ag, Au, Ba, Bi, Br, Co, Cr, Cu, Hf, Ir, Mn, Mo, Ni, Rb, Sb, Sc, Se, Sn, Sr, Ta, W, Ze, Zn, radioactive U and Th (Matl and Wagner 1995; Kabata-Pendias and Pendias 1999; Wagner 2001).

Thus far, standards have not been developed for permissible concentrations of harmful elements in coal and coal-bearing rocks. Therefore, the existing standards for permissible maximum concentrations in water and soil were used (Ordinance ME 2011, 2016).

Studies of the concentration distributions of certain harmful elements in Polish lignite and hard coal and ash have been conducted by Parzentny (Parzentny 1989), Matl and Wagner (Matl and Wagner 1995), Wagner (Wagner 2001), Gmur and Kwiecińska (Gmur and Kwiecińska 2002), Święch and Kwiecińska (Święch and Kwiecińska 2003), Hanak and Kokowska-Pawłowska (Hanak and Kokowska-Pawłowska 2006), Goldsztejn (Goldsztejn 2007), Bielowicz (Bielowicz 2010, 2013), Całus-Moszko and Białecka (Całus-Moszko and Białecka 2013), and Strzałkowska (Strzałkowska 2021). However, in most of these studies,

no significant exceedances of permissible maximum concentrations of toxic elements were found in the investigated materials.

Studies of selected elements, including harmful elements, in rocks coexisting with coal seams have been reported by Hanak et al. (Hanak et al. 2011), Kokowska-Pawłowska and Nowak (Kokowska-Pawłowska and Nowak 2013), and Krzeszowska (Krzeszowska 2017, 2019), among others. Kokowska-Pawłowska (Kokowska-Pawłowska 2018) investigated the concentrations of elements in rocks coexisting with coal seams of the Zaleskie Beds (405) and Ruda Beds s.s. (408) in various lithologies in the vicinity of seven USCB mines. The study found that the average concentrations of elements such as As, Co, Cd, Be, Zn, Pb, Th, U, Sb and Zr in claystone, mudstone, and sandstone were generally comparable to average concentrations in the Upper Continental Crust. However, enrichment in these elements was typically found in coal shales and siderite claystone.

Numerous studies have been conducted globally on the concentrations of toxic elements in sedimentary rocks. The concentrations of these elements are most often compared to their content in the Upper Continental Crust (Taylor and McLennan 1985) or to their Clarke values for a given lithology (Taylor and McLennan 1985; Rudnick and Gao 2004; Ketris and Yudovich 2009).

Clarke values for black shale represent the global average trace-element concentrations in black shales. Black shales (carbonaceous, mainly marine sedimentary rocks) are often enriched with U, V, Mo, Re and many other trace elements. Clarke values for coal similarly represent the global average concentrations of trace elements in coal deposits. Coal Clarke values are a scientific benchmark used for a variety of geochemical comparisons, e.g. between a given coal deposit and global geochemical background (Ketris and Yudovich 2009).

Much of the research that has been conducted has addressed concentrations of toxic elements in black shales. Most of these shales were clearly enriched in elements such as Cd, Co, Mo, Ni, As, Pb and Zn. These elements occur in these rocks mainly in the form of sulfides, but are also present in organic matter (Yudovich and Ketris 2015; Liu et al. 2017; Zanin et al. 2016).

The Zunyi region of Guizhou Province in southern China has black-shale deposits enriched in many elements, including Mo and Ni. Significant amounts of toxic elements such as Mo, Ni, As, Cd, Zn, Cu and Pb leach into the soil from these slate piles during storage. High concentrations of these elements have been documented, frequently exceeding their average concentrations in global soils (Bowen 1979; Coveney and Nansheng 1991; Pašava et al. 2003).

In China, the geochemical mapping of soils around the Yangtze River catchment area showed anomalous geochemical levels of Cd at toxic concentrations (Cheng et al. 2005). In Switzerland, carbonate rocks of the Jura Mountains were found to have high concentrations of Cd along with elevated concentrations in local soils (Quezada-Hinojosa et al. 2009; Liu et al. 2017). In Korea, black-shale weathering released Cd, thus increasing Cd concentrations in soils to as much as 5.7 ppm (Park et al. 2010). In California, USA, soils formed from shale

primary material had elevated concentrations of Cd of up to 22 ppm, with a mean concentration of 8 ppm (Burau 1981; Lund et al. 1981).

Most global shale deposits are enriched with various PTEs, particularly Mo, Zn, Ni, Cr, Cu, V, Co, Pb, U and Ag (Vine and Tourtelot 1970). In certain cases, the concentrations of some of these elements are high enough that they are economically viable to mine (Gustavson and Williams 1981; Plumlee et al. 1999).

The source of PTEs may therefore be the natural bedrock from which they are released into the soil and water environment as a result of weathering (Zeng et al. 2011). Often, however, the sources of toxic elements in soils, other than rocks (e.g. black shales) with enriched concentrations, include wastes from mining and metallurgy (Luo et al. 2009, 2013, 2017; Jacob et al. 2013).

2. Materials and methods

The samples tested in this study represent sedimentary rock of a Carboniferous coal-bearing series from a borehole in the central area of the USCB. Drilling was conducted in this area to obtain geological data on coking coal deposits. The present study used data for 120 samples from borehole WSx (Figure 1). The entire profile is dominated by claystones (seventy-five samples). The other samples were classed as siltstones (twenty-three samples) and sandstones (twenty-two samples). The samples from this borehole represent Zaleskie layers and Orzeskie layers within the Mudstone Series (Westphalian A, B) (depth 482–1300 mbs).

Sample preparation and analysis was conducted by The Bureau Veritas Mineral Laboratory (Vancouver, Canada). Toxic elements were analyzed using inductively-coupled plasma mass spectrometry (ICP/MS) following four-acid digestion ($HF + HClO_4 + HCl + HNO_3$). Major and minor element oxides were determined using X-ray fluorescence methods followed by $LiBO_2/LiB_4O_7$ fusion.

This study analyzed PTEs that may adversely affect the natural environment, including Be, Sc, V, Cr, Co, Ni, Cu, Zn, As, Rb, Sr, Zr, Mo, Cd, Sn, Sb, Ba, W, Tl, Pb, Bi, Th and U.

3. Geochemical analyses of the sedimentary rocks of the Carboniferous coal-bearing series

The samples collected for the study mainly comprised claystones, mudstones and sandstones, with lesser amounts of carbonate rocks (siderites and dolomite inserts) (Figure 1).

The chemical composition of the samples from the coal-bearing and carbon-bearing series of the USCB varied among the samples (limnic series) (Table 1), as shown by the minimum and maximum concentrations of chemical components as well as the standard deviations. The major oxides SiO_2 and Al_2O_3 were the dominant constituents, with contents
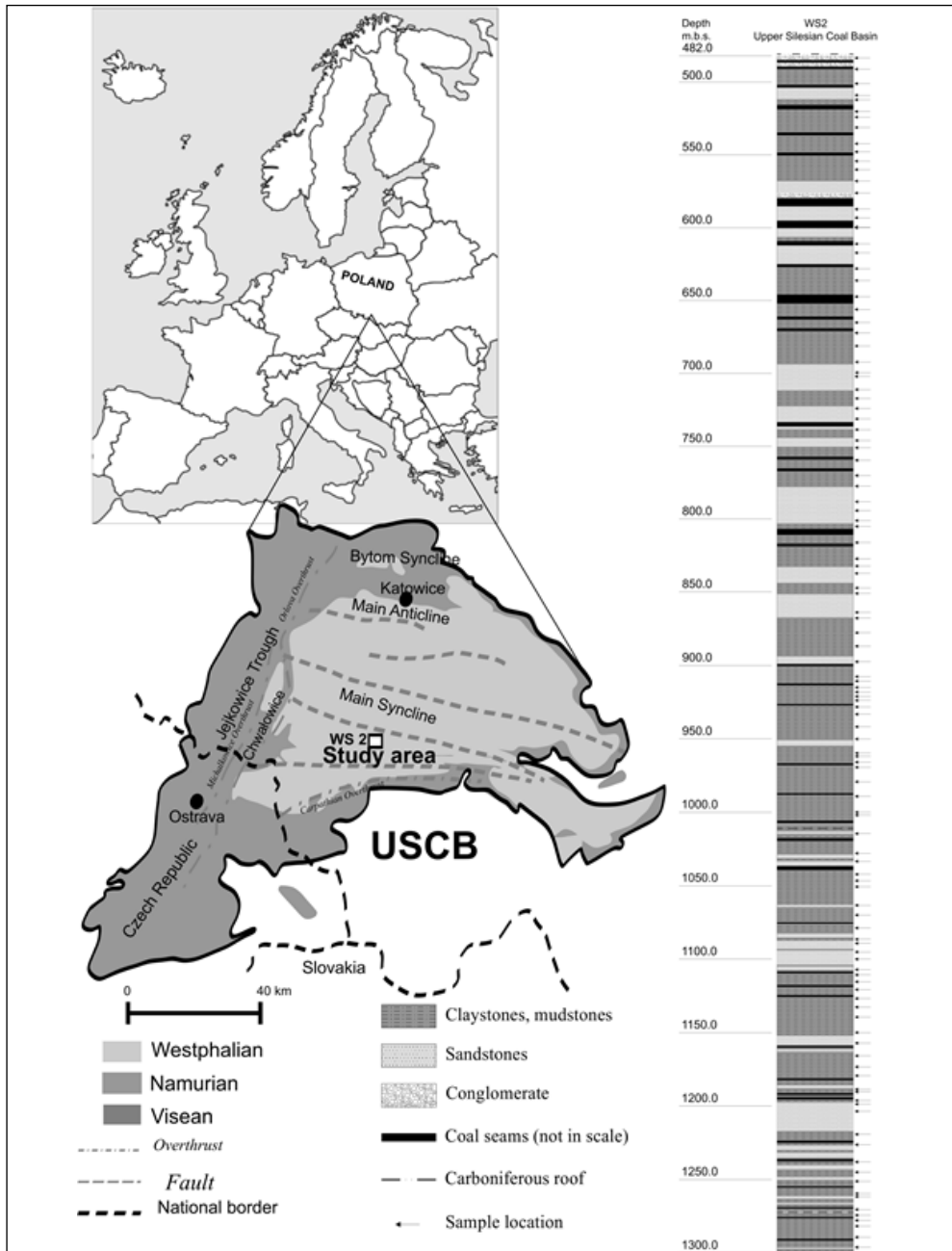
Fig. 1. Schematic of the Upper Silesian Coal Basin and location of the study area
(modified from Jureczka and Kotas 1995; Kędzior 2015) with a simplified profile of the Westphalian
for the Upper Silesian Coal Basin

Rys. 1. Schematyczna mapa Górnośląskiego Zagłębia Węglowego z lokalizacją obszaru badań
oraz uproszczonym profilem westfalu Górnośląskiego Zagłębia Węglowego

ranging from 23.50 to 90.18% and from 4.68 to 27.28%, respectively (Table 1). The Fe_2O_3 content varied, ranging from 1.09 to 32.85%. High Fe_2O_3 concentrations were usually accompanied by an increase in MgO and CaO contents, due to the presence of siderites and dolomite inserts. Other major oxides, such as CaO, K_2O, TiO_2, MgO, Na_2O, and P_2O_5, were also present in lower concentrations. Loss-on-ignition (LOI) content ranged from 1.90 to 24.70%.

Table 1.   Geochemical composition

Tabela 1.   Skład chemiczny

Major oxides	Detection level	Average value ($n = 120$)	Range of results		Standard deviation	Median
			min.	max.		
Al_2O_3 (%)	0.01	18.68	4.68	27.28	5.49	20.37
SiO_2 (%)	0.01	60.59	23.50	90.18	10.88	58.85
Fe_2O_3 (%)	0.04	4.94	1.09	32.85	4.87	3.77
CaO (%)	0.01	0.23	0.06	1.78	0.26	0.16
Cr_2O_3 (%)	0.002	0.02	0.00	0.03	0.004	0.02
K_2O (%)	0.01	3.04	0.94	5.32	0.82	3.15
MgO (%)	0.01	1.37	0.17	6.79	0.94	1.19
MnO (%)	0.01	0.08	0.01	0.37	0.07	0.06
Na_2O (%)	0.01	0.60	0.23	1.17	0.24	0.56
P_2O_5 (%)	0.01	0.11	0.03	0.64	0.09	0.09
TiO_2 (%)	0.01	0.93	0.13	1.30	0.27	1.02
LOI (%)	0.01	9.18	1.90	24.70	3.91	8.80

Concentrations of the analyzed toxic elements in the samples from the coal-bearing series of the USCB are presented in Table 2 and Figure 2. Most elements, such as B, Sc, V, Cr, Ni, Cu, Zn, As, Sb, W, Tl, Pb, Bi, Th and U had higher mean concentrations than those of the Upper Continental Crust (UC) (Table 2).

The average concentrations of Sr, Zr, Mo, Sn and Ba were clearly lower than in the UC. Elements such as Be and Cd had mean concentrations similar to the UC, although slightly enriched or depleted. In the following analyses, toxic elements with concentrations that were clearly lower than the mean in the UC have been omitted.

Knowing the concentrations of PTEs found in sedimentary rocks from mining is important from an environmental point of view. This is particularly the case when there are high concentrations in rocks that may become waste materials. Concentrations of selected

toxic elements, which have higher mean concentrations than those of the UC, are shown in Figure 2. The mean and standard deviations of the concentrations of PTEs in the profile of the Carboniferous coal-bearing series were determined.

Table 2.　　Concentration of toxic elements

Tabela 2.　Koncentracje pierwiastków toksycznych

| Toxic elements (ppm)	Detection limit	Upper Continental Crust (UC) (Taylor and McLennan 1985)	Minimum permissible levels in soils (Ordinance ME 2016)	Average value (n = 120)	Range of results		Standard deviation	Median
					min.	max.		
Be	1.00	3.00	no data	3.00	1.00	7.00	1.25	4.00
Sc	1.00	13.60	no data	17.00	2.00	26.0	5.91	17.00
V	1.00	107.00	no data	114.0	14.00	184.0	38,75	123
Cr	1.00	85.00	200	111.00	11.00	162.0	29,93	118
Co	0.20	17.00	30	17.61	3.00	74.50	12.49	12.45
Ni	0.10	44.00	100	46.50	8.00	187.00	26.20	42.00
Cu	0.10	25.00	150	29.40	3.00	50.00	11,02	32.00
Zn	1.00	71.00	300	110.09	20.00	295.00	45.52	111.00
As	1.00	1.50	20	7.90	1.00	39.00	6.22	5.00
Rb	0.10	112.00	no data	131.90	31.00	239.00	42.71	133.00
Sr	1.00	350.00	no data	108.00	39	270	32.00	109.00
Zr	0.10	190.00	no data	112.78	29.60	169.50	26.71	119.20
Mo	0.10	1.50	25	0.50	0,10	1,80	0,33	0.40
Cd	0.10	0.10	2	0.20	0.10	1.10	0.15	0.20
Sn	0.10	5.50	20	4.60	0.90	8.80	1.50	5.00
Sb	0.10	0.20	no data	0.91	0.30	4.80	0.49	0.80
Ba	1.00	550.00	300	509.00	197.00	761.00	55.00	518.00
W	0.10	2.00	no data	2.50	0.40	4.00	0.81	3.00
Tl	0.50	0.75	no data	1.02	0.50	3.40	0.35	1.00
Pb	0.10	17.00	100	28.41	12.80	65.80	8.28	27.05
Bi	0.10	0.13	no data	0.50	0.20	1,40	0.19	1.00
Th	0.10	10.70	no data	13.11	3.50	21.70	3.72	13.35
U	0.10	2.80	no data	4.78	1.10	7.30	1.35	5.10
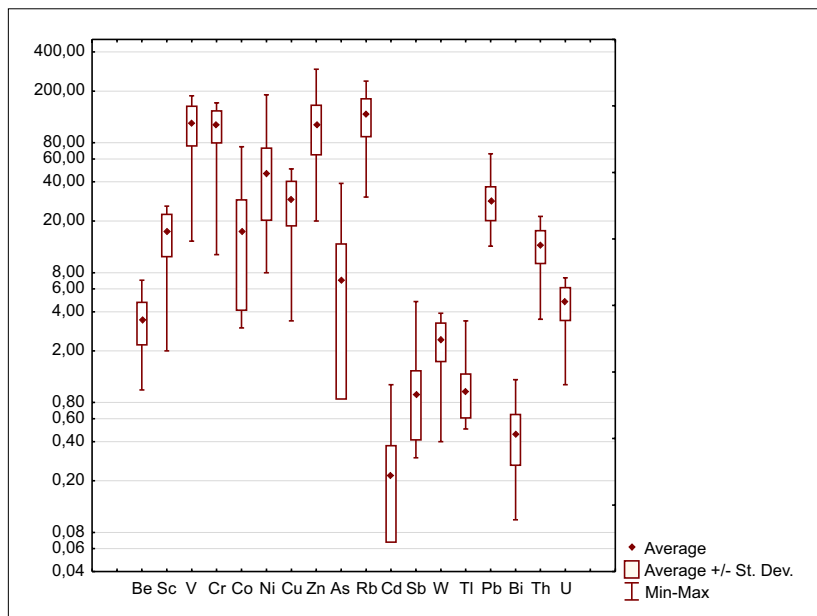
Fig. 2. Concentrations of selected toxic elements

Rys. 2. Zawartości wybranych pierwiastków toksycznych

4. Results and discussion

4.1. Analysis of toxic elements in the sedimentary rocks

The variability in the concentrations of the elements in the profile is presented using average values for individual sections (intervals) of the profile. Taking into account the length of the profile (800 m) and the large number of samples, the profile was divided into intervals of 100 m in thickness. Each of the sections is represented by fifteen samples classified into different lithological types (claystones, siltstones, and sandstones). The share of individual lithological types in the separated parts of the profile (except the depth 700–800 m) is similar, with the clear dominance of claystones (usually about ten samples). The samples from a depth of 700–800 m mainly represent sandstones (eight samples), with a smaller share of claystones and siltstones. The variability in the average concentrations of toxic elements in the intervals is presented in Figure 3.

Highly toxic elements such as Cd and As are readily soluble during weathering processes, and Cd also migrates easily into the environment (Bojakowska 2009; Lei et al. 2010; Jacob et al. 2013; Tabelin et al. 2018; Kubiert et al. 2019). This can cause significant increases

in the concentrations of these elements in soil and water (Ostrowska 2008; Bielowicz 2013; Liu et al. 2017). During weathering, Cd and As are easily activated and adsorbed by clay minerals (mainly illite), iron and aluminum hydroxides, and organic matter. These elements are also strongly bound by sulfides (Kabata-Pendias and Mukherjee 2007; Kabata-Pendias 2010; Yu et al. 2014; Liu 2017). It can be assumed that the average Cd concentration in clay sediments is ~0.3 ppm, while that of As is ~13 ppm (Kabata-Pendias and Mukherjee 2007).

Significant differences can be seen in Cd and As concentrations between sedimentary rocks in Poland and worldwide. In the Polish Lowlands with Paleogene and Neogene forma-tions, the mean Cd content in lignite was higher (~3.0 ppm) and the mean As concentration (~5.0 ppm) was lower than in the analyzed samples (Bielowicz 2013). Globally, high concen-trations of As occur in black coal shales, in which the mean concentration is ~30 ppm (Ketris and Yudovich 2009).

Concentrations of Cd and As in the studied rocks were variable, as indicated by their standard deviations (Table 2, Figure 2). The Cd concentrations in the analyzed samples ranged from 0.10 to 1.10 ppm, while the arsenic concentrations ranged from 1.0 to 39.0 ppm (Figure 2). The mean concentrations of Cd were slightly higher than in the UC (0.20 ppm) and As concentrations were also higher (7.9 ppm) (Table 2). Concentrations of Cd and As in the profile did not covary among the intervals. Weak correlations between the elements can be seen in the lower portion of the profile (Figure 3a and 3b).

Th and U are radioactive elements. These actinides have similar ion radii and coexist in many minerals, often in greater amounts in sedimentary rocks. U is mainly associated with organic matter and with apatite and calcite, while Th is mainly associated with clay minerals (Zanin et al. 2016). During weathering, U has considerable geochemical mobility, as it is easily soluble and moves into the environment. However, Th tends to be captured by secondary products of weathering. Most bituminous shales show high enrichment of these elements (up to 0.7%) (Swanson 1960; Zanin et al. 2016).

U and Th concentrations in Carboniferous black shales from the Lower and Middle South Wales carbon field have been investigated. In these shales, mean values for U and Th were 4.0 and 12.3 ppm (Bloxam 1964). Concentrations and distributions of U and Th in rocks of the "normal" and "anomalous" sections of the Upper Jurassic–Lower Cretaceous Bazhenov Formation in the West Siberian marine basin have also been measured. Sediments of silica-clay rocks were characterized by high concentrations of U (66.5 ppm) and moderate concentrations of Th (5.0 ppm). High concentrations of Th and U were found in mudstones with levels of 11.68 and 11.00 ppm, respectively. However, in clayey-silty sediments, the concentrations of these elements were 2.15 and 3.78 ppm, respectively (Zanin et al. 2016). Enrichment of radioactive elements has also been found in Polish lignite from the Turów and Bełchatów deposits (Bielowicz 2010; Kwiecińska and Wagner 1997). The maximum concentrations of Th and U were 10.8 and 6.3 ppm, respectively.

The mean concentration of Th in the UC (10.70 ppm) is about four times that of U (2.80 ppm) (Taylor and McLennan, 1985). However, in the studied rocks, the mean concentrations of Th and U were clearly higher than in the UC at 13.11 and 4.78 ppm, respectively (Table 2).
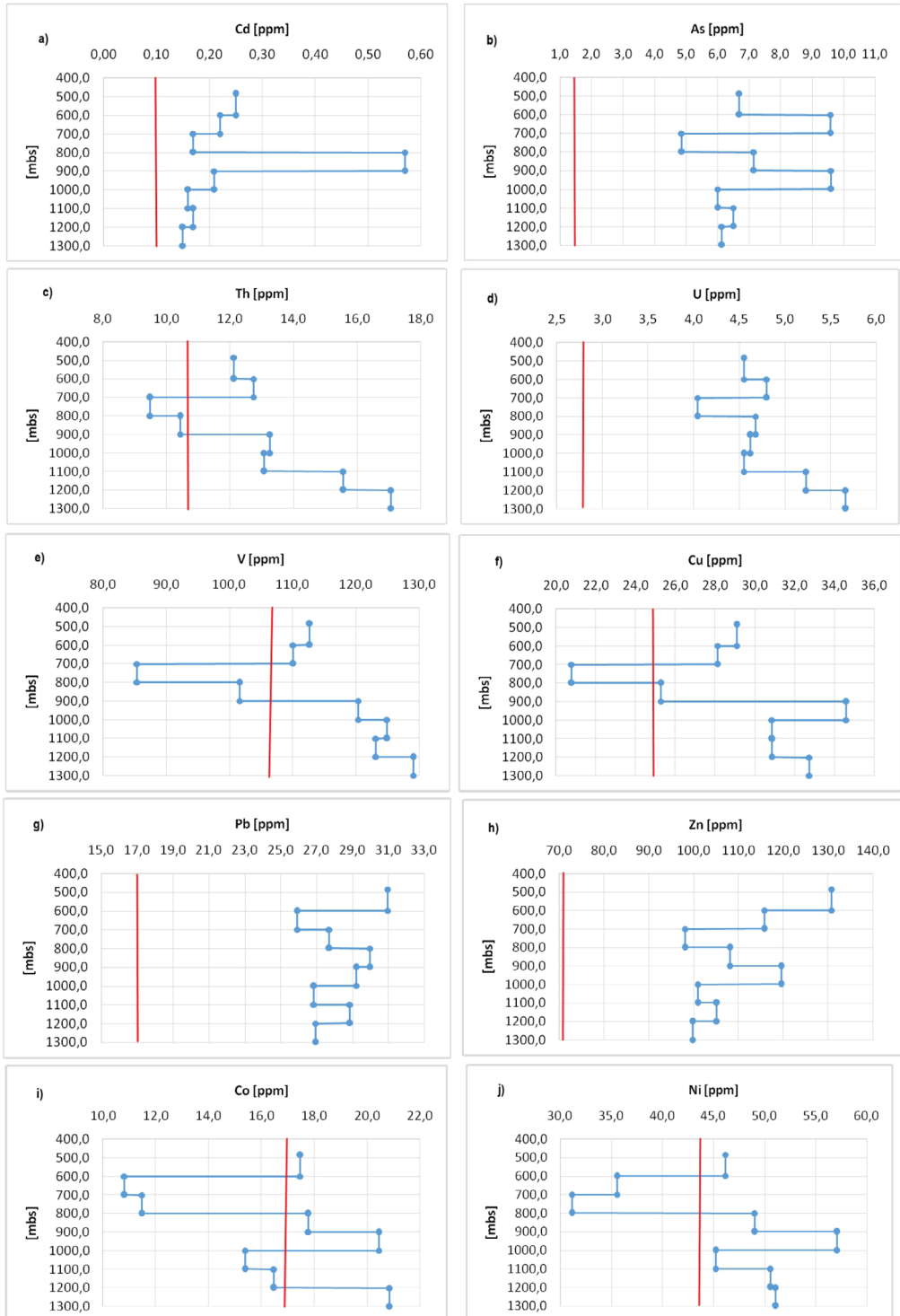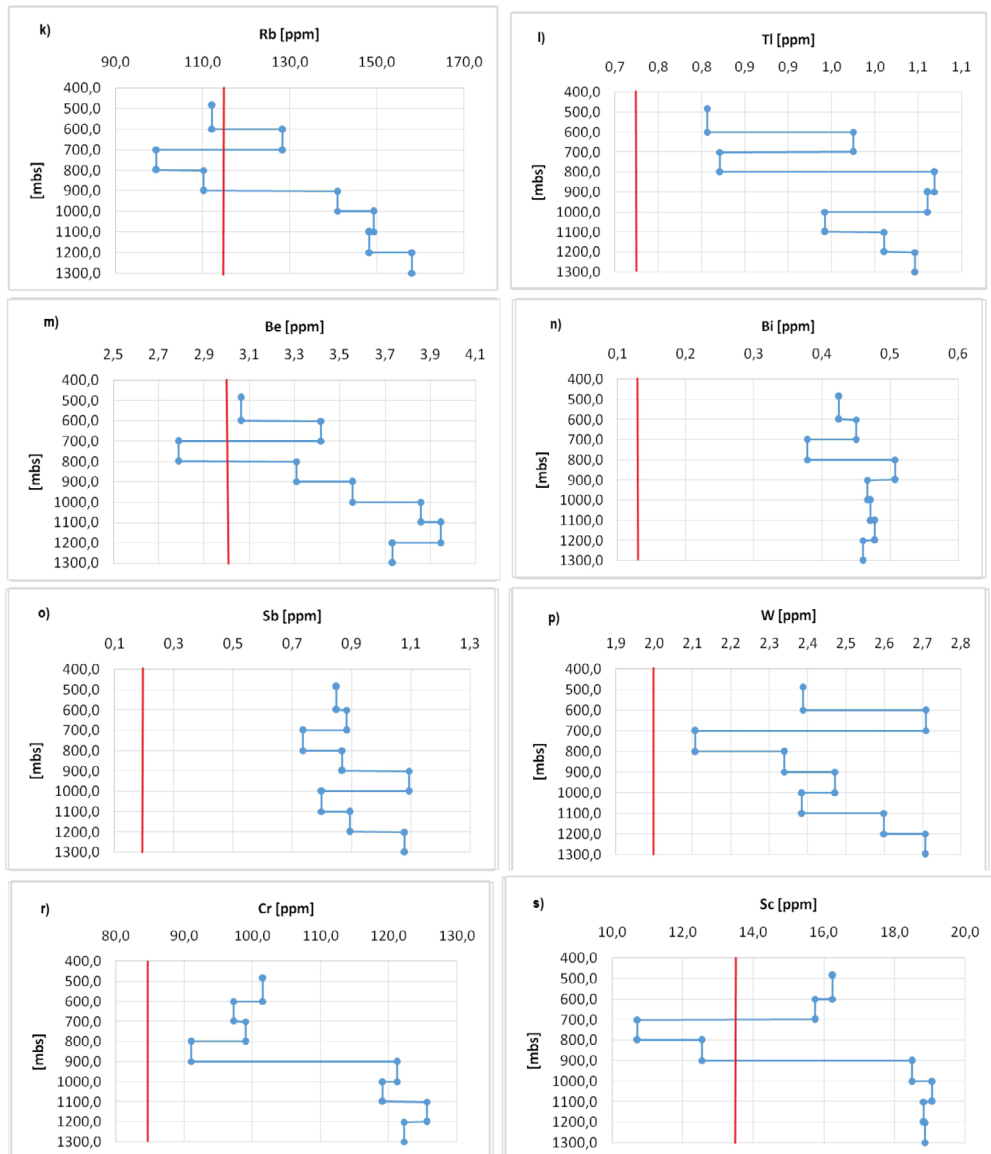
Fig. 3. Stratigraphical variability of average toxic-element concentrations within the borehole WSx
from the Upper Silesian Coal Basin represented by intervals
Explanation: — average toxic-element concentration in the upper continental crust (UC) (ppm)

Rys. 3. Zmienność stratygraficzna średnich stężeń pierwiastków toksycznych w otworze WSx
z Górnośląskiego Zagłębia Węglowego przedstawiona w interwałach
Wyjaśnienie: — średnie stężenie pierwiastków toksycznych w górnej skorupie kontynentalnej (ppm)

The concentration ranges of Th (3.50–21.70 ppm) and U (1.10–7.30 ppm) are shown in Figure 2. The median in both cases was comparable to the arithmetic mean. The observed variabilities of Th and U concentrations in the profiles were similar (Figure 3c and 3d). The mean concentration of Th in the intervals was in some cases lower than in the UC.

In sedimentary rocks, U and As are often found with V and Cu (Vind 2019). V accumulates in large amounts in clay sediments and is often found in pyroxenes, amphiboles (hornblende), biotite and magnetite. It is easily sorbed by clay minerals, Fe compounds, and organic matter. The sorption capacity of clay minerals for Cu increases from kaolinite to montmorillonite (Kabata-Pendias 2010). Cu is mainly found in sulfide minerals.

Fe and Mn hydroxides and organic matter also play an important role in Cu sorption processes. Cu sorption can be reduced by the presence of various organic compounds on the surfaces of minerals. In a hypergenic environment, Cu is easily oxidized. As a result of weathering processes, Cu enters surface waters, where it is present in an ionic form and easily migrates in solution. It can be absorbed into soils where it often accumulates in significant amounts (Kabata-Pendias 2010). In lignite in the Polish Lowlands, the concentration of copper ranges from 2.05 to 71.50 ppm (Bielowicz 2013).

The Cu concentration in the analyzed samples ranged from 3.0 to 50.0 ppm, while the V concentration ranged from 14.0 to 184.0 ppm. Large standard deviations indicate high variability in Cu and V concentrations (Table 2, Figure 2). The observed concentration distributions of Cu and V in the profile were similar (Figures 3e and 3f). The mean concentrations of V and Cu were higher than the concentrations of these elements in the UC (Table 2).

Be is also a highly toxic element. The concentration of Be, generally cited as the "geochemical background", is 2.0 ppm for both soil and rock (Kabata-Pendias and Mukherjee 2007). In hypergenic processes, Be is not very mobile and its minerals are resistant to weathering. Be can only go into solution when present in an isomorphic admixture in silicates. Be is easily absorbed by organic substances; therefore, it is often found in coal seams. In lignite, its average concentration is 1.2 ppm (Ketris and Yudovich 2009). In lignite ash in the Polish Lowlands, concentrations of Be ranging from 0.2 to 9.3 ppm have been found. The highest average concentrations of Be were found in coal ash from the Turów deposit (8.75 ppm) (Bielowicz 2013).

Typical concentrations of Be in soils, rocks, and coal are less than 5 ppm (Benedict et al. 2022). In coaly shales and coal in Bulgaria, mean Be concentrations are highly variable, ranging from 0.9 to 35 ppm. In deposits with enhanced Be content, Be is predominantly organically bound, whereas the inorganic form prevails in deposits whose Be concentrations approximate that in the upper continental crust. Be enrichment in some of the Bulgarian deposits is attributed to subsynchronous coal deposition due to hydrothermal and volcanic activity. This process can increase coal concentrations by up to 14.5 times (Eskenazy 2006).

The Be concentration in the analyzed samples ranged from 1.0 to 7.0 ppm. The average concentration of this element was generally comparable to its concentration in the Upper Continental Crust (3.0 ppm) (Table 2, Figure 2); only one interval had a Be concentration lower than in the UC (Figure 3m).

Other elements classified as harmful are Pb and the slightly less toxic Zn. In sedimentary rocks, Pb mainly occurs in clay minerals (e.g., kaolinite), feldspars, mica, and sulfides, as well as in organic matter (Schalscha et al. 2008; Lei et al. 2010). Zn is mainly a component of sulfide and carbonate minerals, which dissolve easily during weathering. Zn migrates easily in solution and precipitates readily only in the presence of sulfide ions. The concentration of Zn in solution can vary due to sorption by aluminosilicates, hydrated iron oxides, and organic matter.

Enriched and differentiated concentrations of Pb and Zn in coal seams result from both primary bioaccumulation in organic matter and secondary absorption. High concentrations are also found in rocks coexisting with coal seams. During weathering of rock-forming minerals, Pb and Zn are easily released from primary silicates such as biotite and are also present in secondary silicates such as clay minerals and hydrated iron oxides and hydroxides (Scrudato and Estes 1975). During weathering, Pb and Zn also undergo separation in minerals originally formed in paragenesis, due to the lower susceptibility of Pb to oxidation processes, as well as the lower solubility of Pb sulfate.

Generally, the mean Pb concentration in sedimentary rocks is 7.0 ppm, and in clay formations, it is 20.0 ppm. However, the mean Zn concentration in sedimentary rocks is 18.0 ppm (Ketris and Yudovich 2009). In lignite deposits in the Polish Lowlands, the Pb concentration in coal ranged from 0.7 to 26.2 ppm and the Zn concentration ranged from 4.01 to 61.9 ppm. The highest Pb concentration was measured in coal from the Turów deposit (mean of 15.2 ppm) (Bielowicz 2013).

The Pb concentration in the studied rocks was variable and ranged from 12.80 to 65.80 ppm, with a mean concentration of 28.41 ppm. Significant variability was also observed in the Zn concentration, which ranged from 20.0 to 295.0 ppm, with a mean concentration of 110.09 ppm. The high variability of the Zn concentrations in the studied rocks is also reflected in the large standard deviation. The mean concentrations of Pb and Zn in the studied samples were clearly higher than the average concentrations of these elements in the UC (Taylor and McLennan 1985). Pb and Zn concentrations in the profile did not covary among the separate intervals. Weak correlations between the elements can be seen in the lower part of the profile (Figure 3g and 3h). In the case of Zn and Cd, similar variability is observed in the profile (Figure 3h and 3a).

The toxic elements Co and Ni have similar geochemical properties and are classified as siderophilic and chalcophilic elements. Among sedimentary rocks, the highest concentrations of Co and Ni have been found in clay minerals within claystones, clay shales, and Cu-bearing shales formed in reducing environments (Migaszewski and Gałuszka 2016). Co and Ni have geochemical affinity to Mg and Fe (similar ionic radii) and are present in Mg-Fe minerals, mainly olivine and pyroxenes, as well as amphiboles and biotite. They also occur in association with Mn minerals and some sulfide minerals (Zanin 2017). At the hydrothermal stage, Ni forms its own minerals, which often coexist with sulfides and sulfur salts of Be, Co, Ag, and U.

The process of weathering separates Co from Ni. Co creates its own minerals, such as erythrite, while Ni creates colloidal hydrosilicates as well as arsenates. Co can be partially

oxidized and easily goes into solution, and is especially mobile in waters with low pH (<5). In the natural environment, Co has a toxic effect, disturbing the natural biological balance in solutions. However, it is a relatively rare and valuable element, so it is important to identify additional methods of recovery (Bożęcka and Sanak-Rydlewska 2018). Ni hydrosilicates are sparingly soluble, but may migrate in the form of colloidal suspensions. Ni is easily bioaccumulated; therefore, significant concentrations are found in coal seams and co-occurring rocks (Goldschmidt 1954).

Black shales are well known for containing elevated concentrations of many metals, including Co and Ni. Metals concentrated in black shales may occur in pyrite, organic matter, and aluminosilicate minerals such as illite. The mean concentration of Co in coaly shales is 19 ppm, and of Ni is 60 ppm (Slack et al. 2017). The concentrations of Ni, Mo, and Co in siliceous clay black shale rocks of the normal sections of the Bazhenov Formation in rocks with the highest pyrite and organic carbon contents are several times higher than the global mean concentrations of these elements in black shales (Zanin 2017).

The concentrations of Co and Ni in the studied rocks showed significant variability, as indicated by the standard deviations (Figure 2). The Co concentrations in the analyzed samples ranged from 3.0 to 74.50 ppm, while the nickel content ranged from 8.00 to 187.00 ppm (Figure 2). The mean concentrations of Co (17.61 ppm) and Ni (46.50 ppm) in the studied rocks were slightly higher than their concentrations in the UC (Table 2). Covariance of Co and Ni concentrations was observed in the profile and the separate intervals (Figure 3i and 3j).

Sb is a sulfophilic and amphoteric element. During weathering, primary Sb minerals are easily oxidized and transform into sparingly soluble oxides. Sb is easily absorbed by hydrated iron, manganese, and aluminum oxides and hydroxides. Under reducing conditions, Sb occurs mainly in the form of sulfides. Sb is also easily sorbed by organic matter. In lignite seams, its mean concentration is ~0.42 ppm (Bielowicz 2013).

In the tested samples, the mean concentration of Sb was 0.91 ppm (Table 2), while its concentration in the UC is on average 0.2 ppm (Taylor and McLennan 1985). Covariance of Sb, As, and Tl was observed in the profile and the interval charts (Figure 3o, 3b, and 3l).

Bi is easily oxidized during weathering processes, but does not readily migrate into the environment. Bi is often present in a highly dispersed form in coal seams (1.0–5.0 ppm), as well as in higher concentrations in graphite shales (~6.5 ppm) and copper shales (~100 ppm) (Kabata-Pendias and Pendias 1999). In the studied samples, the mean Bi concentration was 0.50 ppm (Table 2), while its mean concentration in the UC is 0.13 ppm (Taylor and McLennan 1985). The mean concentrations of Bi in the intervals of the profile were consistently higher than in the upper continental crust (Figure 3n).

Rb and Tl have a similar ionic radius to K; therefore, they accumulate mainly in minerals and rocks where the K concentration is high (e.g. mica and feldspar) (Burmistrz et al. 2018). During hypergenic processes, they are easily solubilized and sorbed by clay minerals and organic matter, resulting in considerable concentrations in clay sediments and coals. At the hydrothermal stage, Tl is also a component of sulfide minerals.

In the studied samples, the mean Rb concentration was 131.90 ppm and the mean Tl concentration was 1.02 ppm (Table 2). These concentrations were higher than those in the UC of 112.0 ppm and 0.75 ppm, respectively (Taylor and McLennan 1985). The mean Tl concentration in the intervals was always higher than that in the UC (Taylor and McLennan 1985). Rb and Tl concentrations in the profile were only weakly correlated in some intervals (Figure 3k and 3l).

Sc often accompanies Fe and Mg minerals through diadochic substitutions and accumulates in clay sediments and coal to ~5.0 ppm (Kabata-Pendias and Pendias 1999). In the studied samples, the mean Sc concentration was 17.0 ppm (Table 2), while its mean concentration in the UC is 13.6 ppm (Taylor and McLennan 1985). The mean concentration of Sc in certain intervals was lower than in the UC (Figure 3s).

Cr in the lithosphere is typically oxyphilic. Lower concentrations are generally observed in sedimentary rocks than in igneous rocks. It is not very mobile during weathering and its basic mineral, chromite, is resistant to weathering. In the studied samples, the mean concentration of Cr was 111.0 ppm (Table 2), while its mean concentration in the UC is 85.0 ppm (Taylor and McLennan 1985). The mean concentration of Cr in the intervals was higher than the mean in the UC (Figure 3r).

W is relatively insoluble and poorly mobile in a hypergenic environment. The concentration of W in sedimentary rocks ranges from 1.0 ppm to 5.0 ppm. In coal, its mean concentration is ~0.75 ppm, and in coal shale, it is ~2.5 ppm. In the studied samples, the W concentration ranged from 0.40 ppm to 4.0 ppm (Table 2), compared to the mean W concentration in the UC of 2.0 ppm (Taylor and McLennan 1985). The mean concentration of W in the intervals was higher than the mean in the UC (Figure 3p).

The diagrams for the profile show an interval between 700 and 800 m in which most of the elements, other than Pb, Co, and Cr, had lower concentrations. These lower concentrations are likely related to the lithology of rocks in the research area. In this interval, a higher proportion of sandstones in relation to claystones and mudstones was observed than in other portions of the profile (Figure 1).

Comparing the mean concentrations of these toxic elements in the studied rocks to their permissible concentrations in soils, it is apparent that they do not exceed the permissible concentrations specified in the standards (Ordinance ME 2016). This applies to standards for both Group I, Residential Land and Group IV, Industrial Land.

5. Statistical methods – Pearson's correlation coefficient

Statistical methods are a frequently used indirect approach for interpreting the modes of occurrence of elements in coal, coal ash, and coal-hosted basement rocks. A properly selected statistical method, correct sample selection, and a sufficiently large sample population are important in geochemical research. Such an approach provides statistically

significant results, allows geochemically correct conclusions, and avoids misinterpretation (Finkelman 1981; Dai et al. 2020; Eskenazy et al. 2010; Geboy et al. 2013; Xu et al. 2020, 2021).

Determination of the Pearson correlation coefficient is the most commonly used correlation method. This approach uses a parametric correlation that depends on the distribution of the data. The Pearson correlation coefficient r measures the strength and direction of linear relationships between two or more random variables and ranges from –1 to 1. A value of 1 is the strongest possible positive correlation, while a value of –1 is the strongest possible negative correlation (Guilford 1954; Bluman 2003). The strength of a relationship based on its r value is typically described as follows: $-0.3 \leq r \leq 0.3$ none or very weak negative or positive, $0.3 < r \leq 0.5$ weak positive, $0.5 < r \leq 0.7$ moderate positive, $r > 0.7$ strong positive, $-0.5 \leq r < -0.3$ weak negative, $-0.7 \leq r < -0.5$ moderate negative, $r < -0.7$ strong negative correlation (Guilford 1954; Moore et al. 2013). Positive correlation coefficients generally indicate a common source of the elements rather than a common mode of occurrence (Finkelman 1981).

All of the studied samples represent the same stratigraphic level, the coal-bearing Carboniferous series of the Westphalian B. The results of the Pearson correlation analysis showed differing relationships among the analyzed toxic elements in these samples (Table 3). Concentrations of Sc, V, Be, Cu, Rb, and W were positively correlated, with r values ranging from 0.70 to 0.93, which may indicate a similar geochemical origin of these elements. Strong positive correlations were also found between Ni and Co ($r = 0.89$), Zn and Cd ($r = 0.70$), V and Bi ($r = 0.73$), and U and Th ($r = 0.78$). Strong positive correlations ranging from 0.71 to 0.92 were also found between U and Sc, V, Cr, Cu, Rb, and W (Table 3).

As, considered a very toxic element, showed no or very weak negative correlations with other elements. Only in the case of As and Sb was there a moderate positive correlation ($r = 0.56$). A weak positive correlation was found with Tl ($r = 0.47$). This confirms the geochemical paragenesis between As, Sb, and Tl (Migaszewski and Gałuszka 2016). A strong correlation is often found between Group V transition metals (As and Sb) due to their similar physical and chemical properties (Greenwood 2003; Schulz et al. 2017).

No correlation was found between Cd and As or between Cd and other elements, except for a strong positive correlation between Cd and Zn ($r = 0.70$) and a moderate correlation with Pb ($r = 0.39$). The correlation between Cd and Zn is related to the geochemical affinity of these elements (Liu et al. 2017).

V and Cu had very strong positive correlations ($r > 0.7$) with each other and with U in the studied samples. Moreover, there was a strong positive correlation between both V and Cu and Sc, Be, Rb, W and Bi ($r > 0.7$). Be was also strongly correlated with Sc, V and Cu ($r > 0.70$) (Table 3).

Zn and Pb have geochemical affinity, but in the studied samples, they had only a moderate positive correlation ($r = 0.58$). Moreover, Zn and Pb and their sulfides are generally also geochemically associated with Cu, Cd, and Sb (Kabata-Pendias and Pendias 1999).

Table 3. Correlation matrix of studied elements for the Upper Silesian Coal Basin samples

Tabela 3. Macierz korelacji badanych pierwiastków dla próbek Górnośląskiego Zagłębia Węglowego

	Be	Sc	V	Cr	Co	Ni	Cu	Zn	As	Rb	Cd	Sb	W	Tl	Pb	Bi	Th	U
Be	1.00																	
Sc	0.78	1.00																
V	0.81	0.93	1.00															
Cr	0.49	0.60	0.66	1.00														
Co	0.25	0.31	0.38	0.23	1.00													
Ni	0.43	0.50	0.57	0.35	0.89	1.00												
Cu	0.70	0.80	0.88	0.69	0.35	0.53	1.00											
Zn	0.14	0.29	0.27	0.13	0.15	0.21	0.40	1.00										
As	−0.13	−0.11	−0.06	0.03	0.23	0.21	0.04	0.08	1.00									
Rb	0.73	0.81	0.86	0.63	0.31	0.47	0.81	0.17	−0.06	1.00								
Cd	−0.10	−0.11	−0.08	−0.14	0.03	0.00	0.08	0.70	0.09	−0.11	1.00							
Sb	0.24	0.29	0.37	0.28	0.66	0.61	0.43	0.14	0.56	0.33	0.02	1.00						
W	0.67	0.72	0.81	0.66	0.22	0.43	0.77	0.26	−0.05	0.76	−0.05	0.29	1.00					
Tl	0.44	0.42	0.50	0.36	0.25	0.36	0.48	0.12	0.47	0.53	−0.03	0.41	0.45	1.00				
Pb	0.31	0.39	0.47	0.29	0.32	0.41	0.56	0.58	0.08	0.36	0.39	0.37	0.40	0.35	1.00			
Bi	0.64	0.66	0.76	0.47	0.26	0.45	0.73	0.12	−0.13	0.69	−0.01	0.30	0.67	0.45	0.57	1.00		
Th	0.43	0.58	0.54	0.61	0.22	0.31	0.58	0.17	0.04	0.66	−0.07	0.27	0.64	0.28	0.26	0.38	1.00	
U	0.66	0.71	0.80	0.72	0.29	0.45	0.80	0.26	0.01	0.76	−0.04	0.36	0.92	0.45	0.45	0.67	0.78	1.00

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Conclusions

Rock material stored as waste is often a prospective resource base. To accurately assess its suitability for use and potential environmental impact, the determination of its geochemical composition is required.

Carboniferous coal-bearing deposits (Westphalian A, B) from the UCSB showed patterns of similar chemical composition. However, concentrations of toxic elements in the studied rocks showed strong differentiation. As there are no relevant standards for concentrations of toxic elements in post-mining waste stored in impoundments, the concentrations of toxic elements were compared to their concentrations in the UC and to the permissible levels in soils.

The studied rocks contained numerous toxic elements, classified as more or less harmful. Strongly toxic elements at any concentration, such as As, Cd, Pb and Be, as well as less harmful elements such as Sc, V, Cr, Co, Ni, Cu, Zn, Rb, Cd, Sb, W, Tl, Bi and radioactive U and Th had higher or similar mean concentrations compared to mean concentrations in the UC. Some intervals showed lower mean concentrations of elements than in the UC, including Th, V, Cu, Co, Ni, Rb, Be, and Sc. However, the mean concentrations in the intervals of the elements Cd, As, U, Pb, Zn, Tl, Bi, Sb, W, and Cr were always higher than in the UC.

Covariances among the mean concentrations of the toxic elements in the intervals in cases with strong correlations illustrate the relationships between the elements very well.

The Pearson correlation coefficients confirmed the interdependence between some elements. A strong positive correlation was found between elements such as Sc, V, Be, Cu, Rb, and W with r values ranging from 0.70 to 0.93. A strong positive correlation between Ni and Co was also observed, as well as between Zn and Cd, and V and Bi. A clear positive correlation was also noted between U and Th and between U and Sc, V, Cr, Cu, Rb, and W. In the case of As, there was generally no or very weak correlations with other elements. Strong correlations occurred between both elements with high concentrations and those with trace concentrations; therefore, it can be concluded that the abundance of the elements does not affect these results.

Concentrations of the analyzed toxic elements in the studied rocks did not exceed permissible values for soils; therefore, they are probably not a potential threat to the environment. However, in order to support this conclusion, research on the release of potentially toxic elements assessed with leaching tests is necessary.

REFERENCES

Benedict et al. 2022 – Benedict, R.T., Lynch, M., Scinicariello, F., Juergens, M., Alman, B., Derrick, H., Diskin, K. and Dalaijamts, C. 2022. Possibility for human exposure to toxic elements. *Toxicological Profile for Beryllium*, Chapter 5. pp.174–210.

Bielowicz, B. 2010. Selected toxic elements in lignite from the "Gubin" lignite deposit. *(Wybrane pierwiastki szkodliwe w węglu brunatnym ze złoża „Gubin"). Inżynieria Środowiska. Uniwersytet Zielonogórski, Zeszyty Naukowe NR 138,* pp. 92–101 (*in Polish*).

Bielowicz, B. 2013. Selected harmful elements in Polish lignite (*Występowanie wybranych pierwiastków szkodliwych w polskim węglu brunatnym*). *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 29(3), pp. 47–59, DOI: 10.2478/gospo-2013-0027 (*in Polish*).

Bloxam, T.W. 1964. Uranium, thorium, potassium and carbon in some black shales from the South Wales Coalfield. *Geochimica et Cosmochimica Acta* 28(7), pp. 1177–1185, DOI: 10.1016/0016-7037(64)90069-9.

Bluman, A.G. 2003. *Elementary Statistics, A step by step Approach*, (2nd ed.). Mc Graw-Hill, N. York, pp. 637.

Bojakowska, I. 2009. Cadmium in mineral resources of Poland and its potential emission in the environment (*Kadm w surowcach mineralnych Polski i jego potencjalna emisja do środowiska*). Protection of the *Environment and Natural Resources* 40, pp. 22–30 (*in Polish*).

Bowen, H.J.M. 1979. *Environmental chemistry of the elements*. Academic Press, London.

Bożęcka, A. and Sanak-Rydlewska, S. 2018. Research of Co^{2+} ions removal from water solution by using ion exchangers . *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 34(3), pp. 85–98. DOI: 10.24425/122583 (*in Polish*).

Burau, R.G. 1983. National and local dietary impact of cadmium in south coastal California soils. *Ecotoxicology and Environmental Safety* 7(1), pp. 53–57, DOI: 10.1016/0147-6513(83)90048-9.

Burmistrz et al. 2018 – Burmistrz, P., Wierońska, F., Marczak, M. and Makowska, D. 2018. The possibilities for reducing mercury, arsenic and thallium emission from coal conversion processes. *IOP Conf. Series: Earth and Environmental Science* 174, pp. 1–9. DOI: 10.1088/1755-1315/174/1/012003.

Całus-Moszko, J. and Białecka, B. 2013. Analysis of the possibilities of rare earth elements obtaining from coal and fly ash (*Analiza możliwości pozyskania pierwiastków ziem rzadkich z węgli kamiennych i popiołów lotnych z elektrowni*). *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 29(1), pp. 67–80. DOI: 10.2478/gospo-2013-0007 (*in Polish*).

Cheng et al. 2005 – Cheng, H.X., Yang, Z.F., Xi, X.H., Zhao, C.D., Wu, X.M., Zhuang, G.M., Liu, Y.H. and Chen, G.G., 2005. A research framework for source tracking and quantitative assessment of the Cd anomalies along the Yangtze River Basin. *Earth Science Frontiers* 12, pp. 261–272 (*in Chinese with English abstract*).

Coveney, R.M. and Nansheng, C. 1991. Ni-Mo-PGE-Au-rich ores in Chinese black shales and speculations on possible analogues in the United States. *Mineralium Deposita* 26(2), pp. 83–88. DOI: 10.1007/BF00195253.

Dai et al. 2020 – Dai, S., Hower, J.C., Finkelman, R.B., Graham, I.T., French, D., Ward, C.R., Eskenazy, G., Wei, Q. and Zhao, L. 2020. Organic associations of non-mineral elements in coal: A review. *International Journal of Coal Geology* 218, pp. 1–20, DOI: 10.1016/j.coal.2019.103347.

Eskenazy, G. 2006, Geochemistry of beryllium in Bulgarian coals. *International Journal of Coal Geology* 66(4), pp. 305–315, DOI: 10.1016/j.coal.2005.07.005.

Eskenazy et al. 2010 – Eskenazy, G., Finkelman, R.B., and Chattarjee. S. 2010. Some considerations concerning the use of correlation coefficients and cluster analysis in interpreting coal geochemistry data. *International Journal of Coal Geology* 83, pp. 491–493, DOI: 10.1016/j.coal.2010.05.006.

Finkelman, R.B. 1981. Modes of occurrence of trace elements in coal. *U.S. Geological Survey*, Open-File Rep. pp. 81–99, DOI: 10.3133/ofr8199.

Geboy et al. 2013 – Geboy, N.J., Engle, M.A., and Hower, J.C. 2013. Whole-coal versus ash basis in coal geochemistry: a mathematical approach to consistent interpretations. *International Journal of Coal Geology* 113, pp. 41–49, DOI: 10.1016/j.coal.2013.02.008.

Gmur, D. and Kwiecińska, B. 2002. Facies analysis of coal seams from the Cracow Sandstone Series of the Upper Silesia Coal Basin, Poland. *International Journal of Coal Geology* 52(1), pp. 29–44, DOI: 10.1016/S0166-5162(02)00101-5.

Goldschmidt, V.M. 1954. *Geochemistry* pp. 730. Oxford: Clarendon Press.

Goldsztejn, P. 2007. Abundances of selected elements in brown coal from Oscislowo deposit in Konin area. *Scientific work of the Mining Institute of the Wrocław University of Technology. Studies and Materials* 118(33), pp. 17–24 [Online:] http://www.miningscience.pwr.edu.pl/.

Guilford, J.P. 1954. Psychometric Methods (2nd ed.), New York: McGraw-Hill, pp. 595.

Greenwood, N.N. 2003. Vanadium to dubnium: from confusion through clarity to complexity. *Catalysis Today* 78, pp. 5–11, DOI: 10.1016/S0920-5861(02)003188.

Gustafson, L.B. and Williams, N. 1981. Sediment-Hosted Stratiform Deposits of Copper, Lead, and Zinc. DOI: 10.5382/AV75.06.

Hanak, B. and Kokowska-Pawłowska, M. 2006. Variability of the trace element contents in the coal lithotypes and their ashes presented on the background of the 630 coal seam profiles (U.S.C.B.) (*Zmienności zawartości pierwiastków śladowych w litotypach węgla i ich popiołach na tle profilów pokładu 630 (GZW)*). *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 22(3), pp. 69–77 (*in Polish*).

Hanak et al. 2011 – Hanak, B., Kokowska-Pawłowska, M. and Nowak, J. 2011. Trace elements in coal shale from 405 coal seam (*Pierwiastki śladowe w łupkach węglowych z pokładu 405*). *Górnictwo i Geologia – Mining and Geology* 6(4), pp. 27–38 (*in Polish*).

Jacob et al. 2013 – Jacob, D.L., Yellick, A.H., Kissoon, L.T.T., Asgary, A., Wijeyaratne, D.N., Saini-Eidukat, B. and Otte, M.L. 2013. Cadmium and associated metals in soils and sediments of wetlands across the Northern Plains, USA. *Environmental Pollution* 178, pp. 211–219, DOI: 10.1016/j.envpol.2013.03.005.

Jureczka, J. and Kotas, A. 1995. Upper Silesian Coal Basin. In: *The Carboniferous system in Poland.* Warszawa: PIG.

Kabata-Pendias, A. and Pendias, H. 1999. *Biogeochemia pierwiastków śladowych*. Warszawa: PWN (*in Polish*).

Kabata-Pendias, A. and Mukherjee, A.B. 2007. *Trace Elements from Soil to Human*. Springer-Verlag, Berlin, 23. DOI: 10.1007/978-3-540-32714-1.

Kabata-Pendias, A. 2010.*Trace Elements in Soils and Plants*". 4th ed. CRC Pres Taylor and Francis Grup (978-4200-9368-1), DOI: 10.1201/b10158.

Ketris, M.P. and Yudovich, Y.E. 2009. Estimations of Clarkes for Carbonaceous biolithes: World averages for trace element contents in black shales and coals. *International Journal of Coal Geology* 78(2), pp. 135–148, DOI: 10.1016/j.coal.2009.01.002.

Kędzior, S. 2015. Methane contents and coal-rank variability in the Upper Silesian Coal Basin, Poland. *International Journal of Coal Geology* 139, pp. 152–164, DOI: 10.1016/j.coal.2014.09.009.

Kokowska-Pawłowska, M. 2018. Mineralogical and geochemical study of rocks coexisting with coal seams 405 (Zaleskie beds) and 408 (Ruda beds s.s.) in Upper Silesian Coal Basin. (*Studium mineralogiczno-geochemiczne skał współwystępujących z węglem w pokładach 405 (warstwy załęskie) i 408 (warstwy rudzkie s.s.) w Górnośląskim Zagłębiu Węglowym*)) (*in Polish*).

Kokowska-Pawłowska, M. and Nowak, J. 2013. Phosphorus minerals in tonstein; coal seam 405 at Sośnica-Makoszowy coal mine, Upper Silesia, southern Poland. *Acta Geologica Polonica* 63(2), pp. 271–281, DOI: 10.2478/agp-2013-0012.

Krzeszowska E. 2017. Geochemical and faunal proxies in the Westphalian A (Langsettian) marine horizon of the Lublin Coal Basin. *Geological Quarterly* 61(4), DOI: 10.7306/gq.1374.

Krzeszowska, E. 2019. Geochemistry of the Lublin Formation from the Lublin Coal Basin: implications for weathering intensity, palaeoclimate and provenance. *International Journal of Coal Geology* 216, pp. 1–12, DOI: 10.1016/j.coal.2019.103306.

Kubiert 2019 – Kubiert, A., Wilkin, R.T. and Pichler, T. 2019. Cadmium in soils and groundwater: A review. *Applied Geochemistry* 108, DOI: 10.1016/j.apgeochem.2019.104388.

Kwiecińska, B. and Wagner, M. 1997. *Typification of qualitative characteristics of lignite from domestic deposits according to petrographic and chemical and technological criteria for the purposes of geological documentation of deposits and mine service* (*Typizacja cech jakościowych węgla brunatnego z krajowych złóż według kryteriów petrograficznych i chemiczno-technologicznych do celów dokumentacji geologicznej złóż oraz obsługi kopalń*). Kraków: CPPGSMiE PAN (*in Polish*).

Lei et al. 2010 – Lei, M., Zhang, Y., Khan, S., Qin, P. and Liao, 2010. Pollution, fractionation, and mobility of Pb, Cd, Cu, and Zn in garden and paddy soils from a Pb/Zn mining area. *Environ Monit Assess* 168, pp. 215–222, DOI: 10.1007/s10661-009-1105-4.

Liu et al. 2013 – Liu, G.N., Tao, L., Liu, X.H., Hou, J., Wang, A.J. and Li, R.P. 2013. Heavy metal speciation and pollution of agricultural soils along Jishui River in non-ferrous metal mine area in Jiangxi Province, China. *Journal of Geochemical Explor*ation 132, pp. 156–163, DOI: 10.1016/j.gexplo.2013.06.017.

Liu et al. 2017 – Liu, Y., Xiao, T., Perkins, R.B., Zhu, J., Zhu, Z., Xiong, Y. and Ning, Z.2017. Geogenic cadmium pollution and potential health risks, with emphasis on black shale. *Journal of Geochemical Exploration* 176, pp. 42–49, DOI: 10.1016/j.gexplo.2016.04.004.

Lund et al. 1981 – Lund, L.J., Betty, E.E., Page, A.L., Elliott, R.A., 1981. Occurrence of naturally high cadmium levels in soils and its accumulation by vegetation. *Journal of Environmental Quality* 10, pp. 551–556, DOI: 10.2134/jeq1981.00472425001000040027x.

Luo et al. 2009 – Luo, L., Ma, Y.B., Zhang, S.Z., Wei, D.P. and Zhu, Y.G. 2009. An Inventory of trace element inputs to agricultural soils in China. *Journal of Environmental Management* 90, pp. 2524–2530, DOI: 10.1016/j.jenvman.2009.01.011.

Matl, K. and Wagner, M. 1995. *Analiza występowania pierwiastków rzadkich, rozproszonych i śladowych w ważniejszych krajowych złożach węgla brunatnego* [In:] Stryszewski M.: *Selective mining of lignite and accompanying minerals along with technical and economic conditions and ecological benefits* (*Eksploatacja selektywna węgla brunatnego i kopalin towarzyszących wraz z uwarunkowaniami techniczno-ekonomicznymi i korzyściami ekologicznymi*). Kraków: CPPGSMIE PAN, pp. 30–44 (*in Polish*).

Migaszewski, Z., Gałuszka, A. 2016. Environmental geochemistry (*Geochemia środowiska*). Wydawnictwo Naukowe PWN (*in Polish*).

Moore et al. 2013 – Moore, D.S., Notz, W.I. and Flinger, M. A. 2013. *The basic practice of statistics* (6th ed.). New York: W.H. Freeman and Company. pp. 654.

Ordinance ME 2011. *Ordinance of the Minister of the Environment of 25 June 2011 on the classification of ecological status, ecological potential and chemical status and the method of classification of the status of surface water* (*Rozporządzenie Ministra Środowiska z dnia 25 czerwca 2021 r. w sprawie klasyfikacji stanu ekologicznego, potencjału ekologicznego i stanu chemicznego oraz sposobu klasyfikacji stanu jednolitych części wód powierzchniowych*) (DZ.U.2011.poz.1475) (*in Polish*).

Ordinance ME 2016. *Ordinance of the Minister of the Environment of 1 September 2016 on the method of assessing the pollution of the earth's surface* (*Rozporządzenie Ministra Środowiska z dnia 1 września 2016 r. w sprawie sposobu prowadzenia oceny zanieczyszczenia powierzchni ziemi*) (DZ.U.2016.poz.1395) (*in Polish*).

Ostrowska P. 2008. Cadmium – occurrence, use and methods of recycling (*Kadm – występowanie, źródła zanieczyszczeń, metody recyklingu*). *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 24(3/3), pp. 255–260 [Online:] https://docplayer.pl/53919700-Kadm-wystepowanie-yrod3a-zanieczyszczen-metody-recyklingu.html (*in Polish*).

Parzentny, H. 1989. Differences in the content and method of binding some elements in the coal of the Upper Silesian Coal Basin in the profile of a single seam (*Różnice w zawartości i sposobie związania niektórych pierwiastków w węglu Górnośląskiego Zagłębia Węglowego w profilu pojedynczego pokładu*). *Przegląd Górniczy* 4, pp. 17–21 (*in Polish*).

Park et al. 2010 – Park, M., Chon, H.T. and Marton, L. 2010. Mobility and accumulation of selenium and its relationship with other heavy metals in the system rocks/soils–crops in areas covered by black shale in Korea. *Journal of Geochemical Explor*ation 107(2), pp. 161–168, DOI: 10.1016/j.gexplo.2010.09.003.

Pašava et al. 2003 – Pašava, J., Kříbek, B., Žák, K., Li, Ch., Deng, H., Liu, J., Gao, Z., Luo, T. and Zeng, M. 2003. Environmental impacts of mining of Ni-Mo black shale-hosted deposits in the Zunyi region, southern China: Preliminary results of the study of toxic metals in the system rock–soil–plant. *Bulletin of Geosciences* 78(3), pp. 251–260. Czech Geological Survey.

Plumlee et al. 1999 – Plumlee, G.S., Smith, K.S., Montour, M.R., Ficklin, W.H. and Mosier, E.L., 1999. *Geologic controls on the composition of natural waters and mine waters draining diverse mineral-deposit types* [In:] *Environmental Geochemistry of Mineral Deposits. Part B: Case Studies*. Chapter 19, pp. 373–432, DOI: 10.5382/Rev.06.19.

Quezada-Hinojosa et al. 2009 – Quezada-Hinojosa, R.P., Matera, V., Adatte, T., Rambeau, C. and Föllmi, K.B. 2009. Cadmium distribution in soils covering Jurassic oolitic limestone with high Cd contents in the Swiss Jura. *Geoderma* 150(3), pp. 287–301, DOI: 10.1016/j.geoderma.2009.02.013.

Różański, Z. 2019. Management of mining waste and the areas of its storage – environmental aspects. *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 35(3), pp. 119–142, DOI: 10.24425/gsm.2019.128525.

Rudnick R.L. and Gao, S. 2004. Composition of the continental crust. *Treatise on Geochemistry* 3, pp. 1–64, DOI: 10.1016/B0-08-043751-6/03016-4.

Schalscha et al. 2008 – Schalscha, E.B., Escudero, P., Salgado, P., Ahumada, P. 2008. Chemical forms and sorption of copper and zinc in soils of central Chile. *Communications in Soil Science and Plant Analysis* 30(3–4), pp. 497–507, DOI: 10.1080/00103629909370220.

Schulz et al. 2017 – Schulz, K.J., Piatak, N.M., and Papp, J.F., 2017. Niobium and tantalum in: Schulz, K.J., DeYoung, J.H., Jr., Seal, R.R., II, Bradley, D.C. (eds.), Critical mineral resources of the United States–Economic and environmental geology and prospects for future supply: U.S. *Geological Survey Professional Paper* 1802, M1–M34, DOI: 10.3133/pp1802M.

Scrudato R.J. and Estes E.L. 1975. Clay-lead sorption relations. *Environmental Geology* 1, pp. 167–170.

Strzałkowska, E. 2021. Fly ash – a valuable material for the circular economy. *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 37(2), pp. 49–62, DOI: 10.24425/gsm.2021.137563.

Swanson, V.E. 1960. Uranium in carbonaceous rocks. Oil Yield and Uranium Content of Black Shales. *Geological Survey Professional*, paper 356-A. [Online:] https://pubs.usgs.gov/pp/0356a/report.pdf.

Święch, F. and Kwiecińska, B. 2003. Heavy metal concentrations in bituminous coal from the "Janina" coal-mine. Libiąż, USCB Poland. *Mineralogia Polonica* 34(1), pp.69–76.

Tabelin et al. 2018 – Tabelin, C.B., Villacorte-Tabelin M., Einstine, I.P., MayumiIto, M.O. and Hiroyoshia, N. 2018. Arsenic, selenium, boron, lead, cadmium, copper, and zinc in naturally contaminated rocks: A review of their sources, modes of enrichment, mechanisms of release, and mitigation strategies. *Science of The Total Environment* 645, pp. 1522–1553, DOI: 10.1016/j.scitotenv.2018.07.103.

Taylor, S.R. and McLennan, S.H. 1985. The Continental Crust: Its Composition and Evolution. *Blackwell*, Oxford, pp. 312.

Vine, J.D. and Tourtelot, E.B. 1970. Geochemistry of Black Shale Deposits: *A Summary Report. Economic Geology* 65, pp. 253–272, DOI: 10.2113/gsecongeo.65.3.253.

Vind, J. 2019. Black Shale as a Potential Vanadium Resource – an Estonian Example. *Geological Survey of Estonia.* Conference: COST ACTION TD 1407 Final Meeting: Technology Critical Elements – Sources, Chemistry and Toxicology, DOI: 10.13140/RG.2.2.23680.07686.

Wagner, M. 2001. *Determination of toxic and harmful elements in coal and its ashes* (*Oznaczanie pierwiastków toksycznych i szkodliwych w węglu i jego popiołach* [In:] Stryszewski M.: *Selective mining of lignite as a method of reducing the harmful environmental impact of elements present in coal and its combustion products* (*Eksploatacja selektywna węgla brunatnego jako metoda ograniczenia szkodliwego oddziaływania na środowisko pierwiastków obecnych w węglu i produktach jego spalania.* Kraków: AGH (*in Polish*).

Xu et al. 2020 – Xu, N., Finkelman, R.B., Xu, C. and Dai, S. 2020. What do coal geochemistry statistics really mean? *Fuel* 267, DOI: 10.1016/j.fuel.2020.117084.

Xu et al. 2021 – Xu, N., Finkelman, R.B., Dai, S., Xu, C., and Peng, M., 2021. Average Linkage Hierarchical Clustering Algorithm for Determining the Relationships between Elements in Coal. *ACS Omega* 6(9), pp. 6206–6217, DOI: 10.1021/acsomega.0c05758.

Yu et al. 2014 – Yu, Ch., Lavergren, U., Peltola, P., Drake, D., Bergbäck, B. and Åström, M.E. 2014. Retention and transport of arsenic, uranium and nickel in a black shale setting revealed by a long-term humidity cell test and sequential chemical extractions. *Chemical Geology* 363, pp. 134–144, DOI: 10.1016/j.chemgeo.2013.11.003.

Yudovich, Y.E. and Ketris, M.P. 2015. Occurrences and Environmental Impacts of Trace Elements // Coal Production and Processing Technology – Boka Raton: CRC Press, *Geochemistry of Coal*. [Chapter] 3, pp. 48–73. [Online:] file:///C:/Users/User/Downloads/Chapter3%20(3).pdf.

Zheng et al. 2011 – Zeng, F., Ali, S., Zhang, H., Ouyang, Y., Qiu, B., Wu, F. and Zhang, G. 2011. The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants. *Environmental Pollution* 159(1), pp. 84–91, DOI: 10.1016/j.envpol.2010.09.019.

Zanin et al. 2016 – Zanin, Y.N., Zamirailova, A.G. and Ede, V.G. 2016. Uranium, thorium, and potassium in black shales of the Bazhenov Formation of the West Siberian marine basin. *Lithology and Mineral Resources* 51, pp. 74–85, DOI: 10.1134/S0024490216010077.

Zanin et al. 2017 – Zanin, Y.N., Zamirailova, A.G., Eder and V.G. 2017. Nickel, molybdenum, and cobalt in the black shales of the Bazhenov Formation of the West Siberian basin *Geochemistry International* 55, pp. 195–204, DOI: 10.1134/S0016702917010116.

TOXIC ELEMENTS IN CARBONIFEROUS SEDIMENTARY ROCKS FROM THE UPPER SILESIAN COAL BASIN

Keywords

toxic elements, geochemistry, Upper Silesian Coal Basin

Abstract

Trace elements contained in rocks, especially those classified as potentially toxic elements (PTEs), can be largely harmful. Knowledge of the geochemical composition of waste is of great importance due to the potential possibility of contamination with these elements in the environment. The paper presents the geochemical characteristics of the sedimentary rocks from the Carboniferous coal-bearing series of the USCB. The present study used data for 120 samples from borehole WSx representing Zaleskie layers and Orzeskie layers within the Mudstone Series (Westphalian A, B). Major oxide concentrations (Al_2O_3, SiO_2, Fe_2O_3, P_2O_5, K_2O, MgO, CaO, Na_2O, K_2O, MnO, TiO_2, Cr_2O_3, Ba) were obtained using an X-ray fluorescence spectrometry. The concentration of potentially toxic elements (Be, Sc, V, Cr, Co, Ni, Cu, Zn, As, Rb, Sr, Zr, Mo, Cd, Sn, Sb, Ba, W, Tl, Pb, Bi, Th, and U) was analyzed using inductively-coupled plasma mass spectrometry. As there are no relevant standards for the content of toxic elements in post-mining waste stored in dumps, the concentrations of elements were compared to their share in the Upper Continental Crust. Most elements, such as B, Sc, V, Cr, Ni, Cu, Zn, As, Sb, W, Tl, Pb, Bi, Th, and U had higher mean concentrations than those of the Upper Continental Crust (UC). Concentrations of the analyzed toxic elements in the studied samples did not exceed permissible values for soils, therefore they are not a potential threat to the environment. The results of the Pearson correlation analysis showed differing relationships among the analyzed toxic elements in the studied samples.

PIERWIASTKI TOKSYCZNE W KARBOŃSKICH SKAŁACH OSADOWYCH GÓRNOŚLĄSKIEGO ZAGŁĘBIA WĘGLOWEGO

Słowa kluczowe

pierwiastki toksyczne, geochemia, Górnośląskie Zagłębie Węglowe

Streszczenie

Pierwiastki śladowe zawarte w skałach, zwłaszcza te zaliczane do pierwiastków potencjalnie toksycznych (PTE), mogą być w dużej mierze szkodliwe. Znajomość składu geochemicznego odpadów

ma duże znaczenie ze względu na potencjalne możliwości zanieczyszczenia środowiska tymi pierwiastkami. W pracy przedstawiono geochemiczną charakterystykę skał osadowych z serii węglonośnej GZW. W niniejszej pracy wykorzystano dane dla 120 próbek z otworu wiertniczego WSx reprezentujące warstwy zaleskie i orzeskie Serii Mułowcowej (westfal A, B). Stężenia głównych tlenków (Al_2O_3, SiO_2, Fe_2O_3, P_2O_5, K_2O, MgO, CaO, Na_2O, K_2O, MnO, TiO_2, Cr_2O_3, Ba) oznaczono metodą fluorescencji rentgenowskiej. Stężenie pierwiastków potencjalnie toksycznych (Be, Sc, V, Cr, Co, Ni, Cu, Zn, As, Rb, Sr, Zr, Mo, Cd, Sn, Sb, Ba, W, Tl, Pb, Bi, Th, i U) analizowano za pomocą spektrometrii mas z plazmą sprzężoną indukcyjnie. Ze względu na brak odpowiednich norm dotyczących zawartości pierwiastków toksycznych w odpadach pogórniczych składowanych na składowiskach porównano stężenia pierwiastków z ich udziałem w górnej części skorupy ziemskiej (UC). Większość pierwiastków, takich jak B, Sc, V, Cr, Ni, Cu, Zn, As, Sb, W, Tl, Pb, Bi, Th i U, miała wyższe średnie koncentracje niż koncentracje w górnej części skorupy ziemskiej Stężenia analizowanych pierwiastków toksycznych w badanych próbkach nie przekraczały wartości dopuszczalnych dla gleb, dlatego nie stanowią potencjalnego zagrożenia dla środowiska. Wyniki analizy korelacji Pearsona wykazały różne zależności między analizowanymi pierwiastkami toksycznymi w badanych próbach.