

## Trace Elements in Popular Coals Burnt in Low Power Boilers

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### ABSTRACT

The aim of the research was to demonstrate differences in the content of trace elements (U, Th, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Cd, Mo, Hg, Pb, W, Ba) in coal mined in Poland and coal imported from Russia, which are widely available on the market. Ecophile, cube and nut were selected for the research. Among them 3 come from Russia and 3 from Poland. The samples were mineralized and the heavy metal content was determined with the use of mass spectrometry with excitation in induced plasma. The research allowed us to conclude that the same carbon grades showed completely different metal contents and depended on the place of origin. The greatest amount of trace elements was found to be found in ecophysics from Poland (durin). Relatively large contamination with trace elements was also found in Polish peach (window) and in Russian walnut. A relatively high content of uranium was found in three samples, including the ecophyses. When burning coal, even of high quality, we expose the environment to the burden of trace elements, including radioactive elements present in their composition. Heavy metals from coal combustion constantly accumulate in the environment and so far no standards have been established for their content in this fuel.

**Keywords:** hard coal, combustion, solid fuels, heavy metals

### INTRODUCTION

In Poland, hard coal is the main fuel that ensures the energy security. This raw material is supplied as primary fuel for the national economy. Nowadays, coal provides a huge amount of electricity and heat, but its first application is to obtain heat in the combustion process [Kamyk et al. 2021]. The availability of solid fuels varies and is unevenly distributed around the world. Due to historical conditions, coal has been and will be the basic energy resource in Poland in the upcoming years. According to Motowidlak (2018), Poland's coal resources will allow it to meet its energy needs at least until 2030. This is not only due to the abundance of the raw material, but also the ease of its transportation and storage [Pietrzyk-Sokulska et al. 2015].

Among the European Union (EU) countries, Poland is the largest owner of hard coal; however, changes taking place in the mining industry have contributed to large losses of deposits and

increased difficulties with its extraction. This is related, among others, to the closure of mines due to the depletion of operable, i.e. extractable, resources. Therefore, the import of hard coal is increasing, mainly from Russia. Russian raw materials of unknown quality are widely available for sale and used, e.g., by residents for individual heating of households. Values of heavy metals emissions into the atmosphere in 2016 from the combustion of solid fuels in the energy production and transformation sector, fuel combustion out of industry and in industry, were estimated based on national analyses, which include official Polish statistics, e.g. energy statistics. The Central Statistical Office (2016) reports that about 43.8 million tons of hard coal were combusted for the needs of the professional energy sector in 2016 and an average of 10.4 million tons for the needs of individual households, which in total amounts to 54.2 million tons. Zinc is characterized by the highest emissions to the atmosphere during coal combustion, followed by lead, and in

descending order: copper, nickel, arsenic, chromium, cadmium and mercury.

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On the one hand, the progressive depletion of coal resources is becoming a problem of energy security and the import of the raw material is on an increasing scale, while on the other hand, the combustion of coal and fuels derived from it is one of the main sources of air pollution. The compounds produced in this process are carbon dioxide, carbon monoxide, nitrogen oxides, sulfur dioxide, hydrocarbons as well as solid particles such as soot, ash, slag and dusts containing harmful trace elements. The vast majority of exhaust gas components pose a threat to the natural environment [Krumal et al., 2019]. The Intergovernmental Panel on Climate Change (IPCC) states that humanity must completely stop combusting carbon by 2050. In addition, a steady reduction in carbon dioxide emissions is required. Dangers of excessive CO<sub>2</sub> primarily include an increase in the global average temperature, which leads to climate change, fluctuations in the weather and, consequently, natural disasters. In addition, polluted air is a huge threat to human health, as it negatively affects the respiratory system,

circulatory system, nervous system and contributes to the formation of many cancers [Malec and Borowski, 2016; Wielgosiński et al. 2017]. The Ordinance of the Minister of Energy of September 27, 2018, on the quality requirements for solid fuels sets the limit for sulfur content in hard coal. However, standards for heavy metals in this fuel have not yet been established.

In the process of combusting the solid fuels, especially coal, gases and dust containing harmful elements get into the atmosphere. Increased ecological awareness and knowledge as well as modern methods allow performing analyses showing certain heavy metal content in the tested material. The elements present in carbon that cause toxicity at any concentration are lead, mercury, cadmium, beryllium and arsenic, while the harmfulness at higher concentrations is caused by zinc, selenium, thallium, tantalum, tin, chromium, antimony, copper, molybdenum, bismuth, bromine, manganese, titanium, tellurium and cobalt, as well as radioactive ones such as thorium and uranium [Bielowicz, 2013]. Small particle diameter dusts are especially dangerous. Fine dust fractions accumulate large amounts of trace elements on their surface, and they more easily penetrate the human body [Ziębik et al., 1999].

The aim of the research was to demonstrate the differences in the content of trace elements in coals mined in Poland and coals imported from Russia, which are widely available on the market.

## MATERIALS AND METHODOLOGY

From the available hard coal assortments, six samples were selected. Eco-pea coal, cubes and walnut were selected for the tests. Among them, three ones come from Russia and three from Poland. The samples were assigned the following numbers: No. 1 – Russian eco-pea (clarin), No. 2 – Polish eco-pea (vitrain), No. 3 – Russian walnut (vitrain), No. 4 – Polish walnut (durin), No. 5 – Polish eco-pea (durin), No. 6 – Russian cube (clarin). Ten samples were taken and mixed to obtain an average sample.

Samples 1 and 6 are clarin coal (semi-glossy with alternating matte and glossy layers). Both were black, but the first one was slightly more intense. Samples 2 and 3 were vitrain, i.e. completely glossy coals. They were distinguished by black and black-gray color, respectively. Samples 4 and 5 were defined as durin, i.e., mat gloss

coals. The first one had a tar-black color, and the second one was brown-black. Before the analyses, the coal samples were homogenized in a ball mill using containers and balls made of zirconium oxide. Then, 250 mg of coal of each sample was weighed and transferred to Teflon containers, 9 cm<sup>3</sup> of nitric(V) acid HNO<sub>3</sub> and 3 cm<sup>3</sup> of hydrochloric acid HCl were successively added, and then mineralized in a Milestone Ethos Easy microwave mineralizer.

The subsequent step was to determine the elements: U, Th, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Cd, Mo, Hg, Pb, W, Ba, using mass spectrometry with excitation in induced plasma (ICP/MS Agilent 8800). Then, the determined elements were grouped according to their position in the Mendeleev table and similar properties.

## RESEARCH RESULTS AND DISCUSSION

As shown in Figure 1, the gallium content in individual coal assortments varied. The highest amount of this element was found in fully mat Polish eco-pea coal (durin), i.e. 22.657 mg/kg. Half of this metal was found in Russian walnut and Russian eco-pea coal, while the least amount was determined in the Russian cube (6.484 mg/kg). Ziębik et al. (1999) reported that the highest gallium content in Polish coals from the Upper Silesian Coal Basin was 30 mg/kg.

The content of germanium in the tested samples varied considerably. The highest amount of this semi-metal was also found in Polish eco-pea coal (durin), which amounted to 49.784 mg/kg and in sample No. 2, in the Polish eco-pea coal vitrain. The eco-pea coal from Russia contained four times less germanium (11.956 mg/kg). The lowest content of this element was found in the Russian coal cube, which was 2.031 mg/kg. Polish walnut contained less semi-metal than Russian walnut, and the difference was 6.2 mg/kg. The increased content of this element in eco-peas could have resulted from the process of producing these fuels because their production ensures a reduction in the ash content, and low-ash coals are characterized by an increased amount of germanium [Aguścik, 2014; Anchim and Piotrowska-Woroniak, 2010]. All eco-peas showed higher concentrations of germanium, while coals of larger assortments (walnut, cube) contained more gallium. Completely mat Polish eco-pea coal contained more of these trace elements than the other assortments. The only exception was lead, but the content of this element was still close to the highest among the tested samples. This may indicate that the durin eco-pea was the least carbonated of all because the greater the amount of elemental carbon in the solid fuel, the less trace elements [Marciniak-Kowalska, 2010]. Coal No. 4, i.e. walnut from Poland was of the best quality. It contained the least lead and small amounts

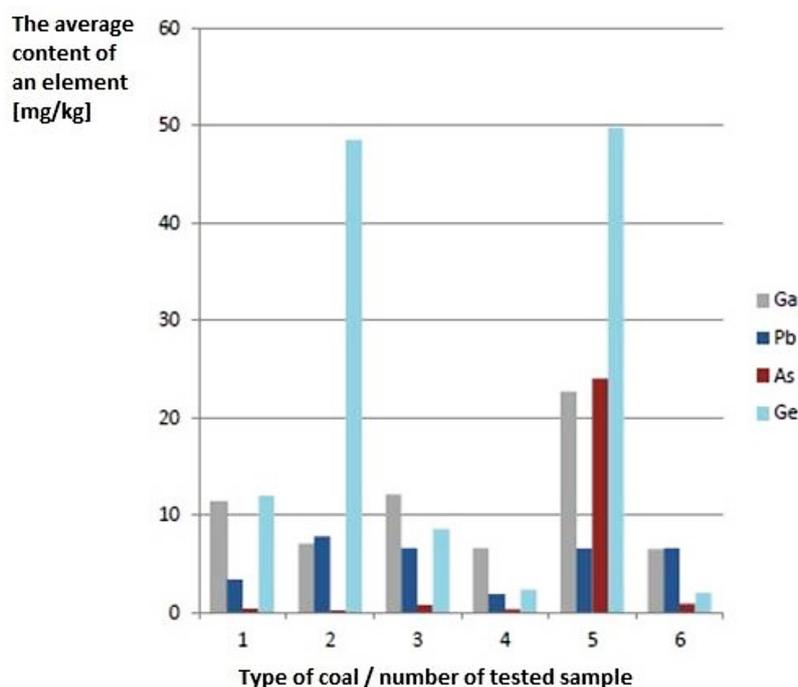


Fig. 1. Gallium, lead, arsenic and germanium content in hard coal samples

of arsenic, gallium and germanium. Coal of the worst quality was Polish eco-pea coal durin. Among this group of elements, lead is the most dangerous because of its harmfulness. Although its content in coal is not as high as, for example, barium or iron, it is a great threat due to its high emission index [KOBiZE, 2018]. Moreover, the retention time of lead in the environment ranges from 400 to 3000 years, so with each subsequent combustion of solid fuels, an increasing amount of this element accumulates in soil, plants, bottom sediments or microorganisms [Pałasz, 2016]. The lowest amount of this element was found in the coal of Polish origin walnut (1.86 mg/kg). The lead content in the remaining coals ranged from 6.5 to 6.6 mg/kg. Bielowicz stated (2013) that there was 15.21 mg/kg of lead in lignite from Szczerców. In turn, Makowska et al. (2017) presented the maximum amount of lead in energetic coals, and it is even 54.7 mg/kg. Another source states that the most lead in hard coal was found in the amount of 50 mg/kg. So far, no standards have been set for the permissible content of trace elements in the coal.

As shown in Figure 1, the Polish eco-pea coal (durin) contained as much as 24.055 mg/kg of arsenic, while the amount of this element in the remaining coals did not exceed 1 mg/kg. Pałasz (2016) included the ranges of content of various trace elements in hard coal and lignite. For hard coal, the maximum arsenic content was 7 mg/kg. In the conducted research, the least amount of arsenic (0.156 mg/kg) was contained in eco-pea coal, also from Poland, but it was different in color and gloss. The remaining coal assortments contained less than 1 mg/kg of arsenic. Arsenic, which gets with dust particles up to 2 $\mu$ m, is transported to the alveoli, causing numerous respiratory ailments. Getting into the bloodstream, it negatively affects the hematopoietic, nervous, reproductive and digestive systems. Combustion of fuels with a significant arsenic content may cause chronic exposure to this element, and it manifests in humans primarily with skin changes and discoloration. The problem is not only arsenic in the dust atmosphere, but also arsenic accumulated in water, soil and food [Medunić et al., 2020].

The common feature of the elements listed in Figure 2 is a small amount of emission into the atmosphere with dust, while their emission in the form of vapor is high. This is mainly due to the low boiling point, which is 356.7 °C for

mercury and 685 °C for selenium. Another factor influencing the behavior of the elements during the combustion of fuels is the melting point of both elements, which is also not high [Ziębik et al., 1999; Bojakowska and Lech, 2015]. Mercury in the environment is toxic at any concentration, and selenium is hazardous when the safe amount is exceeded [Bielowicz, 2013].

Figure 2 shows the content of mercury and selenium in selected hard coal assortments. Among the tested coal samples, the Russian walnut contained the highest amount of mercury, i.e. 0.410 mg/kg. The lowest amount of the element, i.e. 0.216 mg/kg, was contained in Polish eco-pea durin. The average mercury content in world coals is about 0.15 mg/kg, while the maximum amount is 1 mg/kg [Ziębik et al. 1999; Bojakowska and Lech, 2015]. Makowska et al. (2017) tested seven coal samples from the Upper Silesian Coal Basin. The authors reported that the coals contained 0.129 mg Hg/kg, on average. Similar results were presented by Kokowska-Pawłowska (2016), who reported the mercury content for shiny coals as 0.1–0.4 mg/kg. In the tested samples, selenium was determined only in the intensely shiny Polish eco-pea coal (vitrain), which was 1.727 mg/kg and in the others, it was below the limit of quantification. The content of this element for hard coals ranges from 0.2 mg/kg to 10 mg/kg, with the world average being about 1.2 mg/kg. Samples from the LZW contained a maximum of 7 mg/kg of this element [Ziębik et al., 1999; Bojakowska and Lech, 2015].

In the next group, transition metals, such as manganese, vanadium, zinc, iron and tungsten, and the rare earth metal, i.e. barium, were combined. Barium and tungsten are in period 6 of the periodic table, while manganese, vanadium, zinc, and iron are in period 4. The common feature of the selected metals is their medium or high share in hard coal among all trace elements. Iron, barium and zinc occur in the highest amounts, and vanadium, tungsten and manganese in the lower ones [Pałasz, 2016; Ziębik et al., 1999].

Due to its location in the periodic table, barium has high chemical reactivity. It is not a highly emissive element, but is present in much more in coal than other trace elements (except iron). In fly ash, its content is also very high and may be over 1500 mg/kg [Dolnickova, 2012]. Among the tested samples, the highest content of this metal was found in the walnut originating from Russia

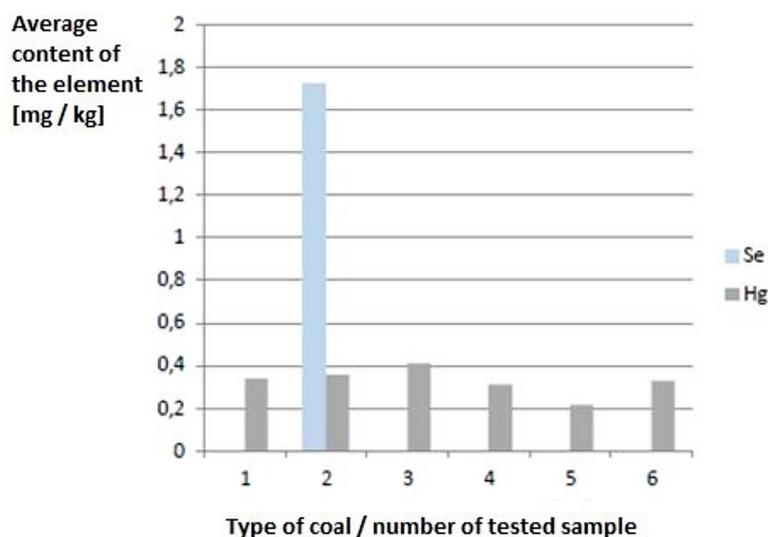


Fig. 2. Selenium and mercury content in hard coal samples

and it was 712.823 mg/kg. The smallest amount of barium was found in Polish eco-pea durin (136.611 mg/kg) as shown in Figure 3. Samples No. 1, 2 and 4 contained more than 500 mg/kg, and sample No. 6 contained over 600 mg/kg. In the world, it ranges from 20 mg/kg to 1000 mg/kg [Ziębik et al., 1999].

Zinc is the element with the highest emission index to the atmosphere. The Central Statistical Office (2016) reported that 54.2 million tons of coal were combusted for the needs of the professional energy sector and for the needs of individual households in 2016. Zinc emission in the same year was 800 tons. This is around 500 tons more than lead emissions [KOBiZE, 2018]. Therefore,

the increased content of this metal in coal poses an even greater threat to the environment and the people living in it. The highest amount of the element was found in sample No. 3, i.e. the Russian walnut, and it amounted to 471.384 mg/kg. Pałasz (2016) reported maximum content of this metal for hard coals at 420 mg/kg. In turn, Makowska et al. (2017) performed an elemental analysis for seven power coals from the Upper Silesian Coal Basin, and the highest zinc content was 199.6 mg/kg. Others stated that the maximum amount of the element in question was 300 mg/kg [Ziębik et al., 1999]. Due to the above data, the Russian walnut can be considered heavily contaminated with zinc. Long-term and constant

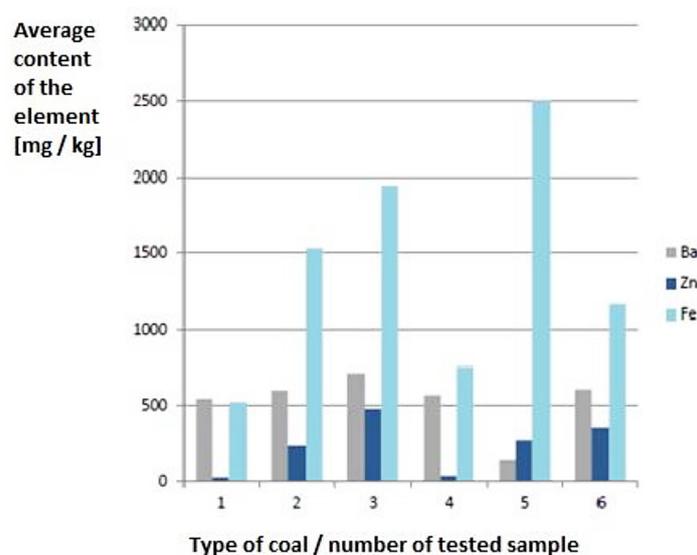


Fig. 3. Barium, zinc and iron content in hard coal samples

combustion of such coal generates large amounts of metal in the atmosphere, and thus, increased bio-accumulation in the biosphere. The lowest zinc content was found in Russian eco-pea coal and Polish walnut. In both eco-peas from Poland, over 200 mg/kg of this element was found.

Iron is an element needed and desired by plants and people because the proper functioning of the body would be disturbed without it. However, just like barium, it has a high accumulation coefficient and, after exceeding a safe standard, becomes harmful, its content increases relating to the geochemical background, and the chemical balance of the biosphere is disturbed [Kabata-Pendias and Pendias, 1999]. The highest iron content, i.e. 2502.272 mg/kg, was found in completely matt Polish eco-pea coal (durin). The least amount of iron was found in sample No. 1, which was Russian eco-pea coal, and it contained four times less iron than in Polish eco-pea coal. The Russian walnut, in which the most barium and zinc was found, was also characterized by a high content of iron (1944 mg/kg), which is shown in Figure 3.

The airborne manganese comes largely from natural dust, and in places free from anthropogenic effects; its content in dust is on average as high as in rocks [Kabata-Pendias and Pendias, 1999]. In areas where coal is combusted, the manganese concentration is higher, which translates into increased bio-accumulation and toxicity. Manganese was most present in sample No. 6, i.e. in the Russian cube (68.659 mg/kg). The Polish walnut

also contained very similar amount of metal, which was 63.874 mg/kg. The lowest manganese content (6.805 mg/kg) was found in sample No. 5, i.e. Polish durin eco-pea, as shown in Figure 4. Kokowska-Pawłowska (2016) tested coals with different lithotype layers. For semi-glossy carbon, the highest manganese content was 119 mg/kg, while the lowest was 77 mg/kg. Other literature presents the amount of the discussed element in coals from the LZW, where the highest metal content was 175 mg/kg [Bojakowska and Lech, 2015]. Comparison of the obtained test results with those presented by other authors allows to conclude that manganese content in the tested coals occurred at a similar, close or lower level.

Only one third of vanadium in the atmosphere originates from natural sources. The rest is dust from industry and fuel combustion [Wang et al., 2019]. At the end of the 1990s, the vanadium concentration coefficient in dust from a large city with developed industry, relating to the composition of the Earth's crust, was 500 on average. For comparison, this coefficient reached the value of 17. Near Stockholm, this metal fell during the year with dust from the atmosphere in the amount of 200 grams per hectare [Kabata-Pendias and Pendias, 1999]. As shown in Figure 4, in the tested samples, the highest concentration of the element was found in Polish eco-pea coal (durin), designated as sample No. 5, and it was 150.47 mg/kg. The average vanadium content in coals in the world is about 24 mg/kg, with the maximum of 100 mg/kg [Bojakowska and Lech, 2015; Ziębik

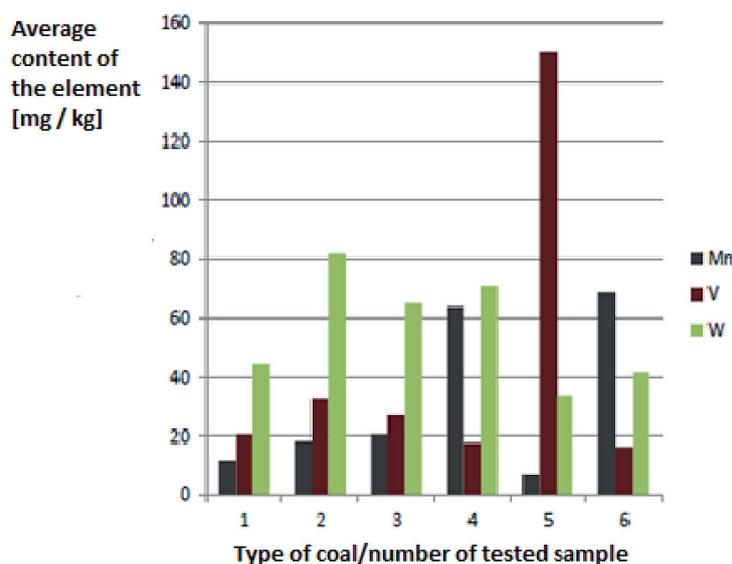


Fig. 4. The content of manganese, vanadium and tungsten in hard coal samples

et al., 1999]. The Russian cube contained nine times less element (and simultaneously, the least of all carbons), which was 16.13 mg/kg. Vanadium at excess concentration in the human body can damage biological structures and have a negative effect on the respiratory and nervous systems [Wang et al., 2019].

The highest amount of tungsten was found in Polish eco-pea coal (vitrain) and it was 81.82 mg/kg. The least amount of the element was determined in sample No. 5, i.e. eco-pea coal also from Poland, but of a different lithotype. Polish and Russian walnut contained similar amounts of metal (65–70 mg/kg), and eco-pea from Russia showed almost the same amount of tungsten as Russian cube (about 44 mg/kg). Yudovich et al. (1985) presented the range of tungsten occurrence in coals from various deposits of the world and it was from 2 mg/kg to 6 mg/kg. Parzenty (2009) also presented results indicating that the content of this metal reached even 200 mg/kg and significantly exceeded the range reported for hard coal from world deposits. However, the mean of all 30 samples examined by Parzenty (2009) was 24 mg/kg. If, together with dust, a significant amount of tungsten gets into vegetables or fruits that are consumed by humans, the nervous system may be disturbed. Mainly the tungsten salts, which are easily soluble, have a negative effect on the human body.

In the subsequent group, transition metals belonging to the 4th and 5th period of the periodic table of elements were compared. Their common feature is medium or low share of all trace elements in coal. Some of them are highly toxic. Cadmium, on the other hand, is dangerous in any amount in the natural environment [Kabata-Pendias and Pendias, 1999].

Copper in coals was on average 17 mg/kg, but the range for hard coals worldwide is 0.5 mg/kg to 50 mg/kg [Kabata-Pendias, Pendias, 1999; Ziębik et al., 1999]. In 2016, 54.2 million tons of coal were combusted, of which the emission during that time reached 240 tons of copper. Although there may be about 160 times less copper than lead in coal, the emissions of both elements are at a similar level [KOBiZE, 2018]. This proves that there is a danger of copper emissions as a result of combusting the solid fuels, even with a low content. Among the assortments selected for the tests, the highest metal content was found in the Russian walnut, i.e. 13.98 mg/kg. Figure 5 shows that Polish eco-pea coal durin

also contained relatively much copper. The smallest amount of this element was found in the walnut from Poland (3.766 mg/kg). Pałasz (2016) presented the range of copper content in carbon in the range of 12–60 mg/kg, while Kokowska-Pawłowska (2016) defined the maximum content at 45.2 mg/kg. The obtained results allow to conclude that the tested samples did not have too high content of the discussed element. However, the retention time for copper in the environment is 860 years, thus frequent combustion of fuels contributes to the constant accumulation of this metal in the ecosystem [Pałasz, 2016]. Moreover, the emission of the element relating to its content in coal is high, which poses a danger to the biosphere.

Although the emission of chromium during the combustion of coal is not high compared to other elements, it constantly accumulates in the atmosphere, soil and water, and its retention time in the environment is 6300 years. This is 6020 years more than cadmium accumulation in the ecosystem. Accordingly, the durability of the metal in question poses a particular danger to animals and humans [Pałasz, 2016]. The highest amount of this element was found in the Polish eco-pea coal (durin) marked as sample No. 5 and it was 8.90 mg/kg. The Russian walnut contained 2.72 mg Cr/kg, and the remaining samples showed less than 2 mg Cr/kg. The average global content of chromium in hard coal is about 15 mg/kg [Bojakowska and Lech, 2015]. Makowska et al. (2017) analyzed trace elements for the same type of solid fuel, in which the minimum amount of chromium was 18.7 mg/kg, and the maximum was 82 mg/kg. The tested coal samples were characterized by a relatively low content of the discussed metal, which was lower than the global average content of chromium in hard coal.

Molybdenum is present in hard coal in a small range (0.1–10 mg/kg) [Ziębik et al., 1999]. In the tested hard coal assortments, the highest metal content was found in the Polish eco-pea coal vitrain, which was 4.45 mg/kg. Very similar content (4.30 mg/kg) was found in Russian eco-pea. As shown in Figure 5, the least of this element was determined in Polish eco-pea (durin). In hard coal from all over the world, molybdenum occurs on average in the amount of 2 mg/kg [Bojakowska and Lech, 2015]. Almost all tested samples showed higher metal content.

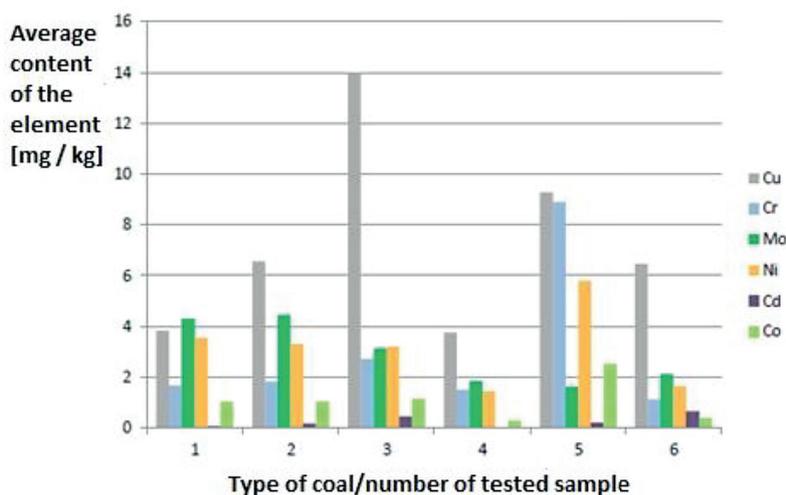


Fig. 5. The content of copper, chromium, molybdenum, nickel, cadmium and cobalt in hard coal samples

The highest amount of nickel, i.e. 5.809 mg/kg, was found in Polish eco-pea coal (durin). The remaining eco-peas contained 3.2–3.7 mg/kg of metal on average, and the least of this element was determined in the Russian cube (1.661 mg/kg). According to Parzenty and Róg (2017), the average global nickel content in coals is 17 mg/kg. In turn, Bojakowska and Lech (2015) determined the range of this metal at 9–76 mg/kg for the tested samples. Due to the above data, the tested assortments were characterized by a low amount of the discussed element.

Cadmium, as shown in Figure 5, is not abundant in hard coal. However, it is toxic at any concentration and, when bio-accumulated into the human or plant body, is hazardous [Bielowicz, 2013]. This metal can remain in the soil environment for 280 years. If soil acidification occurs, previously immobile cadmium becomes a soluble form, which is easily absorbed by plants. Among the analyzed hard coal assortments, the highest amount of cadmium was found in the mat-shiny Russian cube and it was 0.657 mg/kg. Relatively high amount of metal (0.451 mg/kg) was also determined in the shiny Russian walnut. The smallest amount of the element (0.035 mg/kg) was found in the Polish walnut. Kokowska-Pawłowska stated that the amount of cadmium in the clarin ranged from 1.3 mg/kg to 1.8 mg/kg. The range of this metal content in most of the coals mined in the world is from 0.1 mg/kg to 3 mg/kg. Analyzing the above information, it was found that the tested samples had an average cadmium content.

Cobalt occurred in a small amount in all analyzed hard coal assortments. The highest amount

of this metal was found in Polish eco-pea coal (durin) – 2.523 mg/kg. The remaining eco-peas and Russian walnut contained about 1 mg/kg of metal, and the least amounts (0.291 mg Co/kg) were found in the Polish walnut. Pałasz (2016) reported that the range of cobalt in hard coal is 4–20 mg/kg. In turn, the range of the content of this metal in coals from around the world is at the level of 0.5–30 mg/kg, and the average world content is about 5 mg/kg [Ziębik et al., 1999; Bojakowska and Lech, 2015].

Thorium and uranium are radioactive elements that belong to the actinides on the periodic table. They are the only ones in this group to have a long half-life. Moreover, they are abundant in the natural environment of the globe as isotopes, e.g.  $U^{238}$  or  $Th^{232}$ , and are readily bio-accumulative [Kabata-Pendias and Pendias, 1999]. The decay product of uranium is radium, which contributes more to cancer formation. Although the remaining trace elements in coal are more toxic, actinides are highly harmful due to their radioactivity [Pałasz, 2016]. As shown in Figure 6, each assortment contained more uranium than thorium. The inverse relationship was found in China, the USA and LZW. In addition, more thorium than uranium has been found in worldwide solid fuels [Bojakowska and Lech, 2015].

When combusting the coal, about 150 tons of uranium are emitted per year. For comparison, copper has a slightly higher emission (about 230 tons/year). Therefore, our concerns should not only be raised by catastrophes, failures of nuclear power plants or radioactive waste generated from reactors, but also actinides contained in dust

from coal combustion. Among the analyzed hard coal assortments, the highest uranium content was found in Polish eco-pea coal (8.702 mg/kg), Russian eco-pea coal (8.669 mg/kg) and Russian walnut (8.056 mg/kg). The average content of this metal in coals in the world is about 2.3 mg/kg. In China, USA and LZW, the amounts of the element were similar to the world average [Bojakowska and Lech, 2015]. On the other hand, Ziębik et al. (1999) presented the maximum uranium content in most coals from around the world at the level of 10 mg/kg. Therefore, samples No. 1, 2 and 3 can be considered quite highly contaminated with uranium. They contained only 1–2 mg/kg less metal, compared to the coals with the highest content of this element in the world. The least uranium was contained in the Russian cube, but its content exceeded the world average amount of uranium in hard coal.

The world average thorium content in hard coal is about 3.2 mg/kg, and the maximum concentration is set at 10 mg/kg, which is the same as for uranium [Ziębik et al. 1999; Bojakowska and Lech, 2015]. The tested samples contained from 3.212 mg/kg to 5.792 mg/kg of metal. As shown in Figure 6, the highest content was determined in sample No. 1, i.e. in Russian eco-pea coal (5.792 mg/kg) and in samples of Russian walnut and Polish eco-pea coal. In each of them, the presence of the element was greater than 5 mg/kg. Thorium content in the Polish walnut was the same as the average amount of this metal in coal in the world. Bojakowska and Lech (2015) reported maximum amount of thorium for the samples from LZW (33.5 mg/kg) with the average of all tested assortments being 4.8 mg/kg.

## CONCLUSIONS

Based on the analysis of the performed tests, it was found that content of trace elements in the tested hard coal samples was significantly diversified. The same assortments showed completely different metal contents and depended on the place of origin. The macroscopic properties of coal (color and gloss) influenced the content of trace elements. In addition, it was found that the highest content of trace elements was determined in eco-pea coal from Poland, with a matte gloss and brown-black color (durin). It showed the highest content of as many as eight metals out of twenty analyzed. Relatively high contamination with trace elements was also found in Polish eco-pea with an intense gloss and black color (vitrain) and in Russian walnut, which was also shiny and had a gray-black color. Polish eco-pea coal durin contained a lot of vanadium (150.5 mg/kg) and arsenic (24 mg/kg). It was found that the maximum world content of these metals was exceeded in this coal. Eco-peas were not of the best quality because they contained more trace elements (even toxic ones) than walnuts or cubes. Whereas Russian walnut contained very high amount of zinc (471.4 mg/kg), exceeding the maximum content of this metal in hard coal from all over the world, which is 300 mg/kg. Russian eco-pea (clarin), Polish eco-pea (vitrain) and Russian walnut had only 1–2 mg/kg less uranium compared to coals with the highest content of this metal in the world. Summarizing the observed dependencies and the analysis of the content of trace elements in carbon fuels analyzed in this study, it was noted that there was more uranium than thorium in each

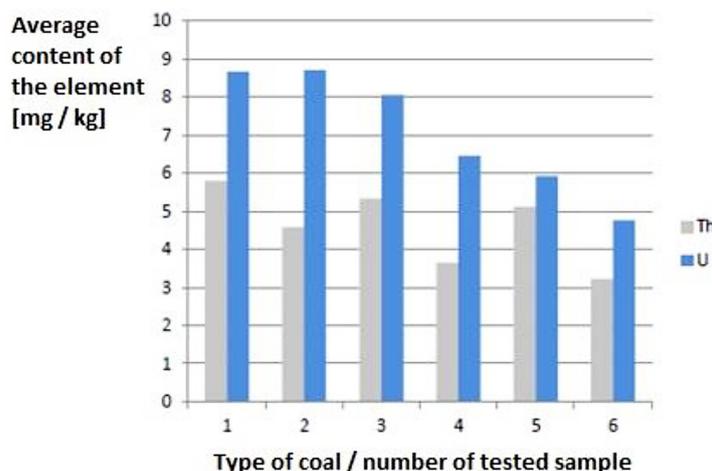


Fig. 6. Thorium and uranium content in hard coal samples

sample. In the results provided by other authors, there was an inverse relationship in Poland and in the world. When combusting the high-quality coal, we expose the environment to the load of trace elements, including radioactive elements present in their composition.

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